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CAMPHORIC ACID: SOME DERIVATIVES OF AMINOLAURONIC ACID.

[FIFTEENTH PAPER.]

BY WILLIAM A. NOYES AND RENE DEM. TAVEAU.

When the nitroso derivative of the anhydride of aminolauronic acid is boiled with an aqueous 10 per cent solution of sodium hydroxide, in the proportion of 1 molecule of the nitroso body to 1.5 molecules of sodium hydroxide, there result, besides the products already described, compounds that have not been obtained under the conditions of decomposition hitherto studied.

The several products of the decomposition and their percentage weight of the nitroso body are, approximately, as follows:

Hydrocarbon, C_9N_{14}	27.8 per cent
Substances volatile with water vapor:	
Isocampholactone, $C_8H_{14}\begin{cases}CO\\O\end{cases}$	21.4 "
An unsaturated acid, $C_8H_{13}CO_2H$	6.6 "

Liquid acids, mainly γ-lauronolic acid(?) 1.4 per cent

Substances not volatile with water vapor:

Impure hydroxylauronic acid, $C_8H_{14}\begin{cases}CO_2H\\OH\end{cases}$ 1.7 "

A new lactone, $C_8H_{14}\begin{cases}CO\\|\\O\end{cases}$ 4.0 "

Briefly stated, the method of obtaining and separating these products was as follows: The nitroso compound, once crystallized from strong alcohol, was introduced into a roomy flask; the required amount of aqueous 10 per cent sodium hydroxide solution added, the flask connected with a return condenser and the contents gently boiled over a free flame until the supernatant layer of hydrocardon was practically colorless, which required about 2 hours.

The method of separating the products of the reaction was essentially the one already described by us[1]; the only modifications necessary were that the hydroxy acid was shaken with strong potassium carbonate solution to separate it from the new lactone, and that the γ-lauronolic acid portion was subjected to a fractional distillation, under diminished pressure, to separate this acid from the crystalline unsaturated acid accompanying it.

Isocampholactone.—This was purified by distilling it under diminished pressure. It boils at 123°.4 (28 mm.) or at 125°.6 (30 mm.). It melts at 32°–33°. An attempt was made to prepare the ethyl ester of the hydroxy acid corresponding to the lactone. It was hoped that by the oxidation of the ester we could obtain the ester of camphononic acid, and thus secure some evidence as to the structure of the lactone. A considerable quantity of the silver salt of the hydroxy acid was prepared as previously described.[2] An analysis of the salt gave 38.62 per cent of silver. Calculated, 38.68 per cent. This salt was allowed to stand for 2 weeks with a large excess of methyl

[1] THIS JOURNAL, **32**, 288.
[2] *Ibid.*, **32**, 290.

iodide and some absolute ether, care being taken to exclude the light. The silver iodide was separated by filtration, and the excess of methyl iodide and ether by distillation under diminished pressure. The product of the reaction, a dark brown oil, was diluted with ether and shaken with a solution of sodium thiosulphate, to remove free iodine which was present. The ether solution was washed with water, dried with calcium chloride and the ether removed under diminished pressure. The product, which was now nearly colorless, was analyzed.

I. 0.1561 gram substance gave 0.3931 gram CO_2 and 0.1273 gram H_2O.

II. 0.1493 gram substance gave 0.3756 gram CO_2 and 0.1220 gram H_2O.

	Calculated for		Found.	
	$C_8H_{14}\langle^{CO}_{O}$	$C_8H_{14}(OH)CO_2CH_3$.	I.	II.
C	70.06	64.45	68.67	68.60
H	9.17	9.76	9.14	9.15

It is evident from the analyses that the product consisted chiefly of unchanged lactone. Thinking that the ester might have been formed at first, and then saponified by the long standing, the mixture was again treated with potassium hydroxide and the silver salt prepared as before. This was boiled for 2 hours with methyl iodide and ether and the product separated as before. It gave now: C, 68.91; H, 9.30.

Methyl Ether of the Hydroxy Acid Corresponding to Isocampholactone, $C_8H_{14}(OCH_3)CO_2H$.—To separate the mixture contained in the above product into its constituents, it was subjected to fractional distillation. The isocampholactone passed over first, leaving a viscous oil, which boiled at about 150°–153° (19 mm.) and solidified on cooling. The compound separates from its solution in isocampholactone in large, compact, beautiful crystals. After solution in sodium carbonate, removal of a small amount of isocampholactone by extraction with ether and reprecipitation with hydrochloric acid, it is deposited in microscopic needles, which melt at 84°.

I. 0.1870 gram substance gave 0.4443 gram CO_2 and 0.1616 gram H_2O.

II. 0.1609 gram substance gave 0.3834 gram CO_2 and 0.1373 gram H_2O.

	Calculated for $C_8H_{14}(OCH_3)CO_2H$.	Found. I.	Found. II.
C	64.45	64.80	64.70
H	9.76	9.69	9.57

0.0889 gram of the substance required for its neutralization 4.76 cc. 0.1 N barium hydroxide. Theory requires 4.78 cc.; 0.1346 gram of the resulting barium salt gave 0.0622 gram $BaSO_4$, corresponding to 27.20 per cent Ba. Calculated for $[C_8H_{14}(OCH_3)CO_2]_2Ba$, 27.07 per cent.

On warming with hydriodic acid in the manner used by Zeisel[1] for the determination of methoxy groups, methyl iodide was eliminated.

While the formation of an ether of the formula given, under the conditions of our experiments, appears very remarkable, the conduct of the compound and the results of the analyses seem to leave no doubt with regard to the nature of the substance.

Substances Volatile with Water Vapor, Other than Isocamphololactone.—These were separated by fractional distillation under reduced pressure, using a Claisen bulb with a delivery tube consisting of two 50 cc. bulbs connected together and to the flask by tubing 1.5 cm. in diameter; tubing of 0.5 cm. diameter connected the bulb farthest from the flask with the rubber tubing to the pump. Such a side tube was found advantageous, owing to the tendency of the new crystalline, unsaturated acid to sublime into and choke the ordinary delivery tube.

After this acid had been distilled, in all, about 10 times, its boiling point was 130°–133° (21 mm.).

The liquid fraction boiled between 137°–150° (22 mm.) and probably consisted largely of γ-lauronolic acid. Its silver salt gave 41.34 per cent Ag. Calculated, 41.33 per cent.

There remained in the distilling bulb, after the liquid por-

[1] Monats. Chem., 6, 789; 7, 406.

tion had passed over, a viscous oil that crystallizes, on long standing, and in a form apparently different from that of the unsaturated acid. The crystals were dissolved in potassium carbonate solution, this solution extracted with ether, then acidified and the acid recovered. It gave a melting point of 90°–90°.5. The amount of this acid was too small for further examination.

The Crystalline Unsaturated Acid, $C_8H_{13}CO_2H$.—This dissolves slowly in cold, concentrated potassium carbonate solution, reduces a cold solution of potassium permanganate instantly and is too readily soluble in the ordinary organic solvents to be recrystallized from them. One-tenth of a gram of the acid neutralized 6.18 cc. of 0.1 N alcoholic potassium hydroxide solution. Calculated, 6.49 cc.

I. 0.1658 gram substance gave 0.4302 gram CO_2 and 0.1347 gram H_2O.

II. 0.2232 gram substance gave 0.5762 gram CO_2 and 0.1818 gram H_2O.

	Calculated for $C_8H_{13}CO_2H$.	Found. I.	II.
C	70.07	70.75	70.40
H	9.17	9.10	9.13

In order to further purify the substance, it was dissolved in very dilute, aqueous potassium hydroxide, and precipitated with dilute sulphuric acid as a snow-white, caseous mass. It was precipitated in this manner 6 times, the first alkaline solution being extracted with ether, and the dissolved ether removed under diminished pressure, before precipitating. It was then twice dissolved in potassium carbonate solution and precipitated as before, the first potassium carbonate solution being extracted with ether to remove any lactones which might be present.

As stated above, the acid boils, or rather sublimes, at 130°–133° (21 mm.). The acid, separated from its calcium salt, melts at 152°–154°. A solution of the acid in a solution of sodium carbonate decolorizes a solution of potassium permanganate instantly.

About 10 years ago Walker and Henderson[1] prepared an acid, which melted at 153°, from the mixtures of esters obtained by the electrolysis of potassium alloethylcamphorate. The acid was obtained from that part of the ester which was most difficult to saponify and which had been boiled for a long time with alcoholic potassium hydroxide. It seems altogether probable that the two acids are identical. It is possible that in both cases the acid was formed by the action of the alkali on γ-lauronolic ("allocampholytic") acid.

Silver Salt, $C_8H_{13}CO_2Ag$.—This was obtained by precipitation from a solution of the sodium salt. The analysis gave 41.48 and 41.35 per cent Ag. Calculated, 41.33 per cent.

Calcium Salt, $(C_8H_{13}CO_2)_2Ca.H_2O$.—This salt separates in large, well formed crystals. It is more soluble in cold than in hot water. The crystals are efflorescent.

I. 0.1924 gram salt lost 0.0088 gram H_2O at 102° and gave 0.0719 gram $CaSO_4$.

II. 0.1774 gram salt lost 0.0080 gram H_2O at 102° and gave 0.0664 gram $CaSO_4$.

III. 0.3430 gram salt lost 0.0170 gram H_2O at 102°.

	Calculated for $(C_8H_{13}CO_2)_2Ca.H_2O$.	Found. I.	II.	III.
H_2O	4.94	4.57	4.51	4.95
Ca	11.01	11.01	11.02	. .

Substances not Volatile with Water Vapor.—The mixture of these products was fractionated under diminished pressure, in order to obtain, especially, the hydroxylauronic acid, if such were present. The boiling point of this acid is given at 180°–185° (25 mm.).[2] The fraction obtained under these conditions was extremely small, amounting to less than 1.5 grams, and was impure, as is shown by the following analyses of the product, the impurity, undoubtedly, being the crystalline body which constitutes, by far the larger part of the mixture.

I. 0.1140 gram substance gave 0.2706 gram CO_2 and 0.0941 gram H_2O.

[1] J. Chem. Soc., 37, 343. The melting point is given in that paper as 158°, but Prof. Walker writes me that this is a misprint. W. A. N.

[2] THIS JOURNAL, 32, 289.

II. 0.1229 gram substance gave 0.2898 gram CO_2 and 0.0998 gram H_2O.

	Calculated for $C_8H_4(OH)CO_2H$.	Found. I.	II.
C	62.73	64.73	64.31
H	9.38	9.20	9.09

The New Lactone, $C_8H_{14}\begin{cases}CO\\|\\O\end{cases}$.—The body is deposited from its solution in ether and by sublimation, in beautiful crystals. Like the crystalline, unsaturated acid, it is too soluble in the usual organic solvents to be recrystallized from them. It does not reduce a neutral solution of potassium permanganate. Fractional distillation, under reduced pressure, was found to be an unsatisfactory method of purification; however, several fractionations of the substance were made, using the Claisen bulb already described. The exact boiling point of the substance was not found, owing to its tendency to sublime. After distilling several times it was observed that at 126° (27 mm.), practically all of the substance had passed over. The pure lactone melts at 164°–165°.

The substance does not dissolve in strong potassium carbonate solution, and shaking with such a solution affords the best method of separation from accompanying acid substances. The following figures were obtained for carbon and hydrogen, they agree best with the formula $C_9H_{14}O_2$.

I. 0.2848 gram substance gave 0.7280 gram CO_2 and 0.2290 gram H_2O.

II. 0.1416 gram substance gave 0.3620 gram CO_2 and 0.1122 gram H_2O.

III. 0.2208 gram substance gave 0.5694 gram CO_2 and 0.1791 gram H_2O.

	Calculated for $C_8H_{14}\begin{cases}CO\\|\\O\end{cases}$.	Found. I.	II.	III.
C	70.07	69.71	69.72	70.33
H	9.17	9.01	8.85	9.09

The lactone is dextrorotatory; 2.0289 grams, dissolved in

absolute alcohol and diluted to a volume of 20 cc., gave, at 22°.4, in a 2 decimeter tube, a rotation of 2°.82 to the right, from which $[\alpha]_D = +13°.87$.

Hydroxy Acid Corresponding to the Lactone, $C_8H_{14}(OH)CO_2H$. —From a solution of the lactone in barium hydroxide, acids precipitate the corresponding hydroxy acid. This melts at 189°.5, with decomposition but no discoloration.

0.1932 gram substance gave 0.4459 gram CO_2 and 0.1576 gram H_2O.

	Calculated for $C_8H_{14}(OH)CO_2H$.	Found.
C	62.73	62.94
H	9.38	9.14

Silver nitrate gives no precipitate in a solution of the potassium salt of the hydroxy acid.

The *barium salt*, $[C_8H_{14}(OH)CO_2]_2Ba.4H_2O$, crystallizes well.

I. 0.2260 gram salt lost 0.0284 gram H_2O at 102° and gave 0.0962 gram $BaSO_4$.

II. 0.2105 gram salt lost 0.0262 gram H_2O at 102° and gave 0.0895 gram $BaSO_4$.

III. 0.3821 gram salt lost 0.0480 gram H_2O at 102°.

	Calculated for $[C_8H_{14}(OH)CO_2]_2Ba.4H_2O$.	Found. I.	II.	III.
H_2O	13.06	12.56	12.44	12.55
Ba	24.90	25.05	25.02	. .

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THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

VIII. REACTIONS WITH α,β-UNSATURATED NITRILES.

BY E. P. KOHLER.

In an earlier paper[1] it was shown that the reaction between α-cyancinnamic esters and Grignard's reagent does not involve

[1] THIS JOURNAL, 33, 333.

the cyanogen group. This result led to the conclusion that the system, C : CC : O, combines with organic magnesium compounds more readily than the system, C : CC ⋮ N, and this conclusion was supported by some preliminary experiments made with α,β-unsaturated nitriles. In continuation of this work, I began a study of the reaction with esters of α-cyancinnamylideneacrylic acid, but the results obtained were so complex that it seemed advisable to make a more careful investigation of the reaction with unsaturated nitriles.

It seems probable that the cyanogen group combines with Grignard's reagent more readily than carbonyl, because Blaise found[1] that it is possible to regulate the reaction with ethyl cyanacetate in such a way that only the cyanogen is attacked :

$$RMgBr + N \vdots CCH_2CO_2C_2H_5 = BrMgN : C(R)CH_2COOC_2H_5 \rightarrowtail RCOCH_2COOC_2H_5.$$

To what extent the properties of the group are modified by the presence of the ethylene linkage is not clear, because very few experiments with unsaturated nitriles have been described ; but the difficulties experienced in hydrolyzing these substances,[2] and in the efforts made to reduce them to the corresponding amines,[3] indicate that the cyanogen in unsaturated nitriles is less reactive than that in saturated compounds.

It is certain that the presence of cyanogen in the α-position greatly increases the apparent reactivity of the ethylene linkage. This is shown by the ease with which unsaturated nitriles are reduced to saturated compounds and, especially, by the fact that these nitriles, like the corresponding unsaturated ketones and esters, readily combine with substances that contain mobile hydrogen. Vorländer found,[4] for example, that in the presence of sodium ethylate cinnamonitrile adds ethyl malonate, according to the equation :

$$C_6H_5CH : CHCN + CH_2(CO_2C_2H_5)_2 = NCCH_2CH(C_6H_5)CH(CO_2C_2H_5)_2.$$

[1] Compt. rend., **130**, 674.
[2] Ann. Chem. (Liebig), **250**, 157.
[3] Ber. d. chem. Ges., **23**, 2859.
[4] Ann. Chem. (Liebig), **320**, 98.

Similarly, Henze[1] obtained the nitrile of symmetrical triphenylglutaric acid by adding benzyl cyanide to α-phenylcinnamonitrile :

$$C_6H_5CH : C(C_6H_5)CN + C_6H_5CH_2CN = C_6H_5CH(CN)CH(C_6H_5)CH(C_6H_5)CN.$$

In all of these cases, however, the primary reaction may consist in 1,4-addition to the conjugated system C : CC ⋮ N, and it was hoped that a study of the reaction between unsaturated nitriles and Grignard's reagent would bring some light on this question.

The experiments described in the present paper were made with cinnamonitrile, α-phenylcinnamonitrile, and β-phenylcinnamonitrile. With the first and last of these, only products similar to those obtained from saturated nitriles could be isolated. Cinnamonitrile and phenylmagnesium bromide, for example, gave benzalacetophenone :

$$C_6H_5CH : CHCN + C_6H_5MgBr = C_6H_5CH : CHC(C_6H_5) : NMgBr \rightarrow C_6H_5CH : CHCOC_6H_5.$$

The results obtained with these substances are, however, not conclusive because, as has been found[2] with nearly all unsaturated compounds having hydrogen in the α-position, the reactions are far from complete and the yields poor.

The experiments with α-phenylcinnamonitrile are much more satisfactory because the reactions are, for the most part, quantitative and it is, therefore, possible to account for all of the material that is used. With ethylmagnesium bromide 98 per cent of the final product consists of stereoisomeric nitriles, formed according to the equation :

$$C_6H_5CH : C(C_6H_5)CN + C_2H_5MgBr + H_2O = C_6H_5CH(C_2H_5)CH(C_6H_5)CN + MgBrOH.$$

It is evident, from this result, that the reagent combines either with the unsaturated carbon atoms or with carbon and nitrogen in the 1,4-positions. The two possible formulas of the magnesium derivatives are, therefore,

[1] Ber. d. chem. Ges., 31, 3059.
[2] This Journal, 34, 568.

$$C_6H_5CH(C_2H_5)C(C_6H_5)(CN)MgBr$$
I.

and

$$C_6H_5CH(C_2H_5)C(C_6H_5) : C : NMgBr.$$
II.

In view of the fact that Grignard's reagent does not combine with unsaturated hydrocarbons,[1] and by analogy with the results obtained with unsaturated esters and ketones, the second formula seems, *a priori*, the more probable one. It was found, however, that the magnesium derivatives obtained from nitriles differ markedly from those obtained from esters and ketones. The latter do not react with simple halogen alkyls, and they give O-alkyl derivatives with the unusually reactive diphenylbrommethane. The former react with ethyl iodide in the cold and the products are C-alkyl derivatives. The magnesium derivative from ethylmagnesium bromide, for example, gives

$$C_6H_5CH(C_2H_5)C(CN)(C_6H_5)C_2H_5.$$

This reaction is exactly like the one that is used for introducing alkyl into substances like cyanacetic ester, malonitrile and benzyl cyanide, by means of metallic derivatives. For these derivatives most writers use a formula analogous to I., but this is done, probably, simply as a matter of convenience, because there is no evidence, that at present can be regarded as valid, in favor of such a formula. Nef[2] has proposed a formula analogous to II. To account for the reactions of ethylsodium cyanacetate, for example, he uses

$$NaN : C : CHCOOC_2H_5$$

and he has succeeded in finding considerable evidence in favor of this arrangement. While this is, in itself, not conclusive, it is supported by all the recent work on tautomerism.

It will be shown, in the experimental part, that most of the reactions of the magnesium derivative can be interpreted on the basis of either formula ; but Formula I. seems improbable

[1] THIS JOURNAL, **31**, 642.
[2] *Ibid.*, **18**, 723. Ann. Chem. (Liebig), **287**, 265.

on more general grounds. This arrangement represents a complex Grignard derivative containing a tertiary alkyl group, and it is highly improbable that such a substance would be formed by addition to unsaturated carbon atoms when the unsaturated compound contains the much more reactive cyanogen group. Moreover, substances of this type cannot be made by treating a tertiary alkyl haloid with magnesium in the usual way. This was established in the present case by treating the corresponding bromine compound with magnesium. No reaction took place until the unusually reactive magnesium of Baeyer[1] was used, and then the product was a mixture of reduction products that did not contain a trace of reactive magnesium.

—The magnesium derivative in question does not behave like a Grignard reagent. It was boiled with acetaldehyde, acetone, ethyl acetate, benzaldehyde and benzophenone, and while the aromatic compounds gave brilliantly colored precipitates, treatment with ice-water in each case resulted in the liberation of unchanged aldehyde, ketone, or ester. These results are not conclusive, because it is known that complex magnesium derivatives do not always react like the simpler substances,[2] but taking all available facts into consideration, I regard Formula II. as the more probable and, therefore, assume that with ethylmagnesium bromide the reaction consists in 1,4-addition.

With phenylmagnesium bromide the same nitrile gives two products—an unsaturated ketone and a saturated nitrile :

$$C_6H_5CH : C(C_6H_5)CN + C_6H_5MgBr = C_6H_5CH : C(C_6H_5)C(C_6H_5) : NMgBr \rightarrowtail C_6H_5CH : C(C_6H_5)C(C_6H_5) : O;$$

$$C_6H_5CH : C(C_6H_5)CN + C_6H_5MgBr = (C_6H_5)_2CHC(C_6H_5) : C : NMgBr \rightarrowtail (C_6H_5)_2CHCH(C_6H_5)CN.$$

This result is evidently not in harmony with Thiele's theory of partial valences.

[1] Ber. d. chem. Ges., 38, 2759.
[2] *Ibid.*, 36, 4272.

EXPERIMENTAL PART.

1. α-Phenylcinnamonitrile and Ethylmagnesium Bromide.

Preliminary experiments showed that the action between the nitrile and alkylmagnesium compounds is not influenced by the conditions under which they are allowed to react, and that the nature of the product is not dependent upon the relative amounts of the reagents. In these experiments both ethereal solutions of ethylmagnesium bromide, made in the ordinary way, and ligroin solutions of ethylmagnesium iodide made according to Tschelinzeff were used. In some experiments the nitrile was added to an excess of the magnesium compound, while in others the magnesium compound was siphoned into an excess of nitrile, and in each case one reaction was carried out at the boiling point of the solvent while another was allowed to proceed slowly, at the temperature of a freezing mixture. The primary product is always a dark red substance that is soluble in ether, but insoluble in ligroin, from which it separates as a paste. On treatment with water it gives ethane, unchanged nitrile and magnesium salts. It is, therefore, a double compound containing the nitrile in place of ether.

When the nitrile is added to boiling solutions this red product disappears almost as fast as it is formed, until the solution contains an excess of nitrile, when it becomes permanent. In the cold the disappearance of the color and the occurrence of the reaction take place very slowly, but the amount of nitrile required to produce a permanent color is the same as in boiling solutions. The product, obtained by treatment with water at this stage, contains no unchanged nitrile. If more nitrile is added, before treatment with water, the color becomes deeper and finally blood-red crystals separate from the solution, but when these are decomposed with water the excess of nitrile is recovered unchanged.

In all subsequent experiments the procedure was as follows: Solid nitrile was added, in small portions, to a boiling solution of ethylmagnesium bromide, until a faint but persistent color appeared in the liquid. The resulting solution, which for brevity will be referred to as the magnesium derivative, was

then treated with the various reagents, as described in the following account :

α,β-Diphenylvaleronitrile, $C_6H_5CH(C_2H_5)CH(C_6H_5)CN$. — The magnesium derivative was poured on cracked ice, the basic salts dissolved with hydrochloric acid and the ethereal layer washed and evaporated in a draught. It first deposited a hard, granular solid and then a considerable quantity of colorless oil. The oil was drawn off with a pump, the solid washed with cold alcohol and repeatedly recrystallized from boiling alcohol. It was thus obtained in small, lustrous crystals, readily soluble in acetone and boiling alcohol, moderately in cold alcohol and ether. The melting point is 115°.

The oil that accumulated in the mother liquors from this solid was dissolved in ether, the solution dried with sodium sulphate and fractioned under diminished pressure. It was thus separated into two substances : The solid previously described, melting at 115° and boiling at 235°–240° (20 mm.) and a colorless oil, boiling at 210°–212° (20 mm.), which remained liquid in a freezing mixture. Both of these substances were indifferent to potassium permanganate in acetone solution—therefore saturated—and a qualitative test showed that both contain nitrogen. The analyses prove that they are isomeric :

I. 0.1560 gram *solid* gave 0.4972 gram CO_2 and 0.1018 gram H_2O.

II. 0.1715 gram *oil* gave 0.5470 gram CO_2 and 0.1158 gram H_2O.

	Calculated for $C_{17}H_{17}N$.	Found. I.	II.
C	86.81	86.91	86.93
H	7.23	7.25	7.45

As α,β-diphenylvaleronitrile contains 2 asymmetric carbon atoms it seemed likely that these two substances represented the two possible racemic modifications. This conjecture was verified by hydrolysis. It was not possible to get more than a trace of acid by boiling either of the substances with alcoholic potassium hydroxide, but complete hydrolysis was obtained by heating them to 180° with concentrated hydrochloric acid, for

4 hours. The result was the same with each substance—a mixture of isomeric acids differing but slightly in solubility in common solvents. The mixture was partially separated by several crystallizations, but sharp melting points were obtained only after many recrystallizations from ligroin.

α,β-Diphenylvaleric Acids, $C_2H_5CH(C_6H_5)CH(C_6H_5)CO_2H$.—The high-melting acid separates from ligroin in very small, lustrous plates, melting at 178°. When free from the lower-melting isomer it is only moderately soluble in ether and very sparingly in ligroin. Analysis:

0.1235 gram substance gave 0.3657 gram CO_2 and 0.0780 gram H_2O.

	Calculated for $C_{17}H_{18}O_2$.	Found.
C	80.30	80.50
H	7.00	7.02

The low-melting acid is also sparingly soluble in ligroin, but it separates from solution much more slowly than its isomer. It is easily recognized in a mixture of the two because it is always deposited in clusters. It is readily soluble in alcohol and ether and it melts at 152°-153°. Analysis:

0.1380 gram substance gave 0.4063 gram CO_2 and 0.0866 gram H_2O.

	Calculated for $C_{17}H_{18}O_2$.	Found.
C	80.30	80.29
H	7.00	7.02

As each of the nitriles, on hydrolysis, gave a mixture of these two acids, it seemed probable that the acids could be mutually transformed by heating with concentrated hydrochloric acid. This was found to be the case. After heating at 180°, for 24 hours, each gave a mixture of the two acids.

α-Ethyl-α,β-diphenylvaleronitrile, $C_6H_5(C_2H_5)CHC(C_2H_5)(C_6H_5)CN$.—The magnesium derivative was treated with a little more than the calculated quantity of ethyl iodide and the mixture boiled for several hours. The resulting clear solution was poured into ice-water and the

product isolated in the usual way. The reaction is a remarkably clean one and 98 per cent of the unsaturated nitrile used in the preparation of the magnesium derivative is contained in the single substance isolated. This was easily purified by crystallization from alcohol or ligroin. It crystallizes in large tabular plates, melting at 105°, readily soluble in acetone, alcohol, ether and chloroform; moderately in ligroin. Analysis:

I. 0.1464 gram substance gave 0.4643 gram CO_2 and 0.1082 gram H_2O.

II. 0.4011 gram substance gave 19.5 cc. N at 21° and 755 mm.

	Calculated for $C_{19}H_{21}N$.	Found. I.	II.
C	86.69	86.49	. .
H	7.98	8.20	. .
N	5.32	. .	5.49

The molecular weight determined in boiling acetone:

$$K = 1710.$$

Solvent. Grams.	Substance. Grams.	Elevation of boiling point.	Molecular weight.
23.00	1.0645	0.316	250
"	1.5865	0.428	251
	Calculated for $C_{19}H_{21}N$,		263

It was extremely difficult to establish the structure of this compound because the cyanogen group does not give any of its usual reactions. That it would be difficult to hydrolyze it could be anticipated from the experiences of E. Fischer[1] and of Victor Meyer[2] with similarly constituted substances. Fischer succeeded in getting triphenylacetic acid by heating its nitrile to 220°–228°, with a mixture of concentrated hydrochloric and glacial acetic acids, but similar treatment of this compound gave only unchanged nitrile. Victor Meyer and his pupils found that it is generally possible to transform refractory nitriles into acid amides by protracted boiling with aqueous alcoholic potassium hydroxide. This was tried, but the sole

[1] Ann. Chem. (Liebig), **194**, 262.
[2] *Ibid.*, **250**, 157.

effect, after boiling for 6 days, was found to be the elimination of a small quantity of cyanogen as potassium cyanide. After vainly trying Gattermann's[1] and Sudborough's[2] modifications of Bouveault's method, all attempts at direct hydrolysis were abandoned.

The nitrile was then treated with Grignard's reagent, in the expectation of getting a ketone that could subsequently be transformed into the acid; but even this reaction, which takes place so readily with simpler nitriles, failed. After boiling for a day with methylmagnesium iodide and phenylmagnesium bromide the entire amount of nitrile was, in each case, recovered.

The structure of the substance was finally established by reduction. Ladenburg's method, using sodium in boiling absolute alcohol, proved inefficient, but when boiling amyl alcohol was substituted for ordinary alcohol the nitrile slowly disappeared and no unchanged substance could be detected after adding 15 times the calculated amount of sodium. The alcoholic layer, on distillation with steam, gave a solid that is much less volatile with steam than amyl alcohol. More of this solid was obtained by fractioning the alcoholic distillate under diminished pressure. The solid was purified by crystallization from ligroin. Analysis:

0.1575 gram substance gave 0.5245 gram CO_2 and 0.1312 gram H_2O.

	Calculated for $C_{18}H_{22}$.	Found.
C	90.8	90.8
H	9.2	9.3

The substance is 3,4-diphenylhexane. It melts at 92°, boils at 175° (20 mm.) and is readily soluble in organic solvents.

The alkaline solution contained all the cyanogen as potassium cyanide, hence the reduction is represented by the equation:

[1] Ber. d. chem. Ges., 30, 1279.
[2] *Ibid.*, 28, 917.

$$C_6H_5(C_2H_5)CHC(C_6H_5)(C_2H_5)CN + H_2 = C_6H_5(C_2H_5)CHCH(C_6H_5)C_2H_5 + HCN.$$

Methyldiphenylvaleronitrile, $C_6H_5(C_2H_5)CHC(CH_3)(C_6H_5)CN$, was made for the purpose of ascertaining whether it would be easier to hydrolyze it than the corresponding ethyl derivative. It crystallizes in prisms, is readily soluble in alcohol and ether, and melts at 99°. Analysis:

0.1311 gram substance gave 0.4160 gram CO_2 and 0.0909 gram H_2O.

	Calculated for $C_{18}H_{19}N$.	Found.
C	86.74	86.54
H	7.62	7.70

All efforts to hydrolyze the substance were unsuccessful.

Benzyldiphenylvaleronitrile, $C_6H_5(C_2H_5)CHC(CH_2C_6H_5)(C_6H_5)CN$.—Victor Meyer and his pupils found it impossible to introduce a benzyl group into benzyl cyanide, in which one hydrogen had previously been replaced by methyl, ethyl, or benzyl. It was of interest, therefore, to determine whether such a group can be introduced by means of the magnesium derivative. It was found that, while the latter reacts more slowly with benzyl bromide than with ethyl iodide, the final result is just as satisfactory, the yield of the new compound being almost the calculated amount. The product of the reaction was poured into water and distilled with steam, to remove excess of benzyl bromide and a small quantity of the ethyl derivative formed from the excess of ethyl bromide used in the preparation of the magnesium derivative. The residue was purified by crystallization from alcohol and benzene. From the latter it crystallized in needles, containing 1 molecule of benzene, which it loses slowly at the ordinary temperature. Analysis:

0.7663 gram substance lost 0.1471 gram at 100°.

	Calculated for $C_{24}H_{23}N.C_6H_6$.	Found.
C_6H_6	19.30	19.21

I. 0.1300 gram substance gave 0.4213 gram CO_2 and 0.0844 gram H_2O.

II. 0.4090 gram substance gave 16.7 cc. N at 23° and 753 mm.

	Calculated for $C_{24}H_{23}N$.	Found. I.	II.
C	88.59	88.39	. .
H	7.10	7.21	. .
N	4.31	. .	4.56

The molecular weight determined in boiling acetone:

$$K = 1710.$$

Solvent. Grams.	Substance. Grams.	Elevation of boiling point.	Molecular weight.
55.0	0.7460	0.074	313
"	1.1505	0.116	300
	1.8370	0.187	306
	Calculated for $C_{23}H_{21}N$,		325

The compound is readily soluble in benzene, acetone and boiling alcohol, sparingly soluble in cold alcohol and ligroin. It melts at 140°.

All of these alkyl derivatives contain two unequal, asymmetrical carbon atoms and are, therefore, capable of existing in two inactive modifications, but only one substance was obtained in each case. It follows that only one magnesium derivative is formed when ethylmagnesium bromide combines with phenylcinnamonitrile, and that the two stereoisomeric diphenylvaleronitriles described above result from the process of decomposing this magnesium derivative with water. It is possible to vary the relative amounts of the isomers, but it has not been feasible, up to this time, to direct the reaction in such a way as to get only one substance.

Benzoyldiphenylvaleronitrile,

$C_2H_5CH(C_6H_5)C(COC_6H_5)(C_6H_5)CN$ or

$C_2H_5CH(C_6H_5)C(C_6H_5) : C : NCOC_6H_5$.—

The magnesium derivative was treated with an equivalent quantity of benzoyl chloride and the mixture boiled for an hour. The product separated in the solid form when the solu-

tion was poured into ice-water. The reaction is a clean one and, like that with halogen alkyls, gives but one substance, which is obtained in calculated quantity. It was purified by crystallization from alcohol, from which it separated in large needles, melting at 137°. It is readily soluble in chloroform, acetone and boiling alcohol, moderately in cold alcohol and ether, very sparingly in ligroin. Analysis:

0.1520 gram substance gave 0.4748 gram CO_2 and 0.0858 gram H_2O.

	Calculated for $C_{24}H_{21}ON$.	Found.
C	85.00	85.18
H	6.12	6.26

The benzoyl derivative does not reduce a solution of potassium permanganate and it is indifferent to bromine. It is very easily hydrolyzed both by acids and bases, the sole products, in each case, being the solid diphenylvaleronitrile and benzoic acid. Although it is not feasible, at present, to distinguish between the two possible formulas written above, the first seems the more probable in view of the relatively low melting point and the fact that only one nitrile is formed on hydrolysis.

The *acid* $C_2H_5CH(C_6H_5)C(C_6H_5)(CN)COOH$ or $C_2H_5CH(C_6H_5)C(C_6H_5) : C : NCO_2H$.—The magnesium derivative absorbed dry carbon dioxide rapidly and passed into a crystalline solid that was insoluble in ether. This was thoroughly washed with anhydrous ether, then suspended in ice-water and cautiously acidified with iced hydrochloric acid. The organic acid separated as an oil, and all efforts to solidify it, or get it in any other form suitable for analysis, failed. That it is a single substance is certain, because it breaks down when warmed and gives, as the only products, carbon dioxide and solid diphenylvaleronitrile. At low temperatures the acid is fairly stable. After standing in an ice chest for several days it still dissolved completely in a solution of sodium bicarbonate. At the ordinary temperature it slowly gives off carbon dioxide and it decomposes instantaneously when dropped into boiling water. The salts are

still less stable than the acid. The solution in sodium bicarbonate became milky with separated nitrile when it was evaporated at 0°, in a vacuum, and when the oil was treated with potassium hydroxide it passed into the solid nitrile, apparently without previously going into solution.

3,4-Diphenylhexanone-2, $C_2H_5CH(C_6H_5)CH(C_6H_5)COCH_3$.—Diphenylvaleronitrile (115°) readily reacts with methylmagnesium iodide. The reaction was studied for the purpose of ascertaining whether it would yield two stereoisomeric ketones. This was found to be the case. One of the ketones separated in the solid form when the product of the reaction was poured into iced hydrochloric acid. The other remained in the ethereal solution and, on evaporation, deposited as an oil. The solid was purified by crystallization from alcohol. It was obtained in stout needles, melting at 116°. It is readily soluble in ether and acetone, moderately in cold alcohol, sparingly in ligroin.

By fractional distillation, under diminished pressure, the oil was separated into two substances, the ketone already described and a new compound that solidified in the receiver. The latter, after crystallization from ligroin, melted at 56°. The analyses show that the substances are isomeric.

I. 0.1443 gram substance (116°) gave 0.4547 gram CO_2 and 0.1012 gram H_2O.

II. 0.1313 gram substance (56°) gave 0.4120 gram CO_2 and 0.09279 gram H_2O.

	Calculated for $C_{18}H_{20}O$.	Found. I.	II.
C	85.71	85.82	85.60
H	7.93	7.76	7.86

The oily modification of diphenylvaleronitrile was also treated with methylmagnesium iodide and, as was to be expected, gave a mixture of the same two ketones.

Diphenylvalerophenone, $C_2H_5CH(C_6H_5)CH(C_6H_5)COC_6H_5$.—Two isomeric ketones are also obtained when either the solid or the oily diphenylvaleronitrile is added to a solution of phenylmagnesium bromide. The high-melting ketone crystal-

lizes in needles, melting at 170°. It was purified by crystallization from a mixture of chloroform and alcohol. It is readily soluble in acetone and chloroform, sparingly in alcohol and ether.

The low-melting ketone crystallizes in plates, melting at 92°. It is readily soluble in alcohol and ether, sparingly in ligroin. It was purified by crystallization from a mixture of ligroin and ether. Analyses :

I. 0.1375 gram substance (170°) gave 0.4443 gram CO_2 and 0.0886 gram H_2O.

II. 0.1234 gram substance (92°) gave 0.3970 gram CO_2 and 0.0783 gram H_2O.

	Calculated for $C_{28}H_{20}O$.	Found. I.	II.
C	87.93	88.05	87.74
H	7.00	7.16	7.05

In view of the results just described and those recorded in an earlier paper,[1] it is probable that a product obtained by Grignard's reaction always contains all possible racemic modifications.

II. Phenylcinnamonitrile and Phenylmagnesium Bromide.

This reaction, as stated in the introduction, always gives rise to two products : triphenylpropionitrile and benzaldesoxybenzoin.

There is no evidence of action when the reagents are brought together at the ordinary temperature ; the solid nitrile dissolves in the ethereal solution of the magnesium compound without production of color and without evolution of heat and, if the clear solution is immediately poured into ice-water, all of the nitrile is recovered. The reaction proceeds slowly, however, even in an ice chest and becomes complete in 4 to 6 weeks. The product, on treatment with ice-water, gives about 20 per cent of unsaturated ketone. The remainder is triphenylpropionitrile.

In a boiling solution of the magnesium compound, the unsaturated nitrile immediately gives rise to a blood-red color

[1] This Journal, 28, 153.

that slowly disappears again on continued boiling. The reaction is complete after 2–3 hours and the product, treated in the usual way, gives 30–40 per cent of unsaturated ketone.

It is difficult to separate the mixture of benzaldesoxybenzoin and triphenylpropionitrile. The best results were obtained as follows: The product of the reaction, diluted with 2–3 times its volume of ether, is poured into iced hydrochloric acid contained in a separating funnel. The magnesium derivative of the nitrile is decomposed at once and most of the nitrile dissolves in the ether, while the magnesium derivative that yields the unsaturated ketone passes into a thick paste which adheres to the ice and the walls of the funnel. By drawing off the ethereal solution immediately, a fairly good separation is obtained.

The paste dissolves slowly when it is shaken with ether and dilute hydrochloric acid. The ethereal solution, on evaporation and dilution with alcohol, first deposits the high-melting modification of benzaldesoxybenzoin and then a small quantity of oil. The ketone was identified by analysis and comparison with a specimen made from benzil. The oil was added to the ethereal solution obtained directly from the magnesium compound. This solution, on evaporation, left an oil that solidified, almost completely, on standing. The solid was recrystallized from methyl alcohol until it melted sharply at 102°. The analysis and reactions given below show that it is triphenylpropionitrile.

The oily residues that accumulated from the mother liquors were dissolved in ether, the solution dried with sodium sulphate and fractioned under diminished pressure. The only substances obtained, after removing small quantities of phenyl bromide and diphenyl, were the two compounds already mentioned.

Triphenylpropionitrile, $(C_6H_5)_2CHCH(C_6H_5)CN$, prepared as just described, crystallizes in plates that melt at 102°. It is readily soluble in alcohol and ether, moderately in methyl alcohol, sparingly in ligroin.

0.1496 gram substance gave 0.4890 gram CO_2 and 0.0935 gram H_2O.

	Calculated for $C_{21}H_{17}N$.	Found.
C	88.26	88.21
H	6.01	6.20

Triphenylpropionamide, $(C_6H_5)_2CHCH(C_6H_5)CONH_2$, was obtained by heating the nitrile to 160°, for 4 hours, with concentrated hydrochloric acid. The small quantity of acid formed at this temperature was removed with sodium carbonate and the residue crystallized from aqueous alcohol. The amide separated in needles, melting at 213°. It is readily soluble in alcohol, moderately in ether, very slightly in boiling water. Analysis:

0.1423 gram substance gave 0.4333 gram CO_2 and 0.0345 gram H_2O.

	Calculated for $C_{21}H_{19}ON$.	Found.
C	83.72	83.44
H	6.33	6.55

By heating the amide at 200° with concentrated hydrochloric acid, it was easy to hydrolyze it to triphenylpropionic acid. This was identified by comparison with a specimen, made by saponifying the ester.

Ethyltriphenylpropionitrile, $(C_6H_5)_2CHC(C_6H_5)(C_2H_5)CN$.—Ethyl iodide was added to a solution of the magnesium derivative obtained with phenylmagnesium bromide, the mixture boiled for 2 hours, and the product separated as described under triphenylpropionitrile. Two substances were obtained: Benzaldesoxybenzoin and a new compound which was purified by crystallization from alcohol and ligroin. Analysis:

0.1220 gram substance gave 0.3964 gram CO_2 and 0.0755 gram H_2O.

	Calculated for $C_{23}H_{21}N$.	Found.
C	88.74	88.58
H	6.74	6.95

Ethyltriphenylpropionitrile is readily soluble in alcohol and

ether, moderately in boiling ligroin. It was obtained in needles, melting at 134°. No change took place when the substance was heated to 200° with concentrated hydrochloric acid.

III. Experiments with Cinnamonitrile and β-Phenylcinnamonitrile.

Cinnamonitrile reacts very readily both with methylmagnesium iodide and with phenylmagnesium bromide. Red, intermediate compounds are formed, but these disappear almost immediately. When the solution obtained with methylmagnesium iodide was treated in the usual way, it gave a dark brown oil. A part of this was tested for nitrogen, which proved to be absent, showing that the cyanogen group is involved in the reaction. The remainder of the oil was repeatedly extracted with low-boiling ligroin. This, on evaporation, deposited a pale yellow, crystalline solid, melting at 42°. A small quantity of the solid was dissolved in alcohol and treated with a few drops of benzaldehyde and sodium hydroxide. In a short time dibenzalacetone, melting at 112°, began to separate, proving that the original substance is benzalacetone. The yield of the unsaturated ketone was small—less than 60 per cent of the calculated amount.

The mixture obtained with phenylmagnesium bromide, treated like that obtained from methylmagnesium iodide, gave about 68 per cent of benzalacetophenone. The residue, insoluble in ligroin, was boiled with an alkaline permanganate solution until no further reduction took place. Any product formed by 1,4-addition of phenylmagnesium bromide to cinnamonitrile would be oxidized to β,β-diphenylpropionic acid by this procedure. The only organic compound obtained was benzoic acid, showing that the reaction involves only the cyanogen group.

The result obtained in a single experiment carried out with β-phenylcinnamonitrile indicates that this substance reacts like cinnamonitrile. The only product obtained with phenylmagnesium bromide was β-phenylbenzalacetophenone, which

was identified by comparison with a specimen on hand. The yield was 68 per cent of the calculated amount.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
January, 1906.

Contributions from the Chemical Laboratory of Case School of Applied Science.

XLVI.—ON THE COMPOSITION OF PETROLEUM.

BY CHARLES F. MABERY.

THE SULPHUR COMPOUNDS AND UNSATURATED HYDROCARBONS IN CANADIAN PETROLEUM.[1]

BY CHARLES F. MABERY AND WILLIAM O. QUAYLE.

In a paper published some time ago by one of us (Mabery) on a preliminary examination of Canadian petroleum,[2] it was stated that 225 liters of sulphur oil from Canadian burning oil was in process of distillation for the purpose of separating the individual sulphur constituents. On account of the pressure of other lines of work, study of those distillates was delayed, but it has been resumed at intervals until the results described in this paper were obtained.

On returning to this work it seemed worth while to ascertain first whether the oil selected really represented constituents of crude petroleum, or whether it consisted, to a greater or less extent, of decomposition products incident to the process of refining. Since the question of decomposition could be determined in sulphur petroleum from any source, a quantity of crude oil from the Lima, Ohio, field was distilled *in vacuo* and the distillate, corresponding to that from which burning oil is prepared, carefully separated and agitated thoroughly with alcoholic mercuric chloride, for the purpose of precipitating the sulphur compounds. The oil was next agitated vigorously with ordinary sulphuric acid, the acid sludge drawn off and diluted with water, carefully avoiding heat so far as possible.

As usual, a dark red oil separated above the solution, but it

[1] The sulphur derivatives of the hydrocarbons described in this paper are evidently members of a new series, differing essentially in composition, physical properties and chemical relations from any of the well-known series of sulphur compounds. For this new series I suggest the name Thiophane. C. F. M.

[2] THIS JOURNAL, 13, 89 (1891).

lacked the heavy sulphurous odor characteristic of sludge as it is ordinarily separated from sulphur petroleum. The odor of this oil resembled that of sludge after the sulphur compounds had been removed, and it showed still greater similarity in its behavior toward bromine, with which it readily united with the evolution of heat, and the formation of an addition product heavier than water, precisely similar to the behavior of sludge products. The precipitate with mercuric chloride resembled, in all respects, the characteristic products which are so useful in separating the sulphur compounds.

As further evidence of the presence of unsaturated hydrocarbons in this oil, a portion of the oil precipitated from sulphuric acid was heated with concentrated hydrobromic acid to 100°, and the product fractionated *in vacuo* to collect, in a smaller limit, the bromine addition product. It was not intended to prepare an individual bromine derivative sufficient for analysis, since this would have been impossible with the small amount to be obtained in this manner, but only to be sure that an addition product with hydrobromic acid could be formed. The higher vacuum distillate gave an abundant reaction for bromine after heating with lime, showing that addition of the acid had taken place. The results of these experiments are described in full, that there may be no misapprehension concerning the source of the sulphur compounds and unsaturated hydrocarbons which will be described in this paper. They confirm the results of similar experiments described in the former paper.

In continuing the distillation of the 225 liters of crude sulphur oil, with the aid of the apparatus elsewhere described, the distillates were carried through entire up to 250° (50 mm.) at first within 5°, during 4 distillations. The lower fractions were then continued within single degree fractions until the lower portions could be distilled under atmospheric pressure. It was not possible to accomplish in this manner more than a general separation, since all the distillates were mixtures, yet the value of the great amount of tedious labor was shown after the separation of the individual constituents, of which the greater portion distilled at approximately the same tempera-

tures as the original distillates; and although it seemed a great expenditure of effort to distil such a large volume of oil in quantities of 10 liters, the capacity of the porcelain still employed, and to continue the distillation of the entire quantity, this seemed to be the only available method for the separation of these peculiar bodies from the crude oil. When first collected, all the fractions were nearly colorless, but on standing they turned dark red, especially those with higher boiling points. The fractions collected below 125° (50 mm.) were found to be exceedingly unstable. On standing from 6 months to 2 years, some of these distillates deposited very dark, heavy oils, doubtless formed from unstable unsaturated hydrocarbons, terpenes, or sulphur compounds by polymerization.

In separating the constituents of the vacuum distillates, we followed, in general, the method described in a former paper. Three or four hundred grams of the oil were shaken in a large flask with an excess of an alcoholic solution of mercuric chloride, which gave a heavy precipitate, crystalline in the lower fractions, a thick, viscous mass in the less volatile and a heavy, oily deposit in the vacuum distillates above 160°. There invariably separated above the alcohol a lighter oil, which contained no sulphur, or at most, analysis showed less than 0.5 per cent. Upon diluting the alcohol more lighter oil collected, which doubtless has a different composition from the other, since, as will appear later, it showed essentially different properties.

In recovering the sulphur compounds from the mercuric chloride precipitates, after thoroughly washing with alcohol and very volatile gasolin, the precipitate was decomposed by hydrogen sulphide, in presence of a considerable volume of alcohol, the mercuric sulphide separated by filtration, washed with alcohol and the alcohol largely diluted. For the most part the lighter oil separated, some remaining in suspension, which collected after standing a short time. With all possible care in washing the mercuric chloride precipitate, a single precipitation was never sufficient to remove all the sulphur-free oil. The percentages of sulphur in the individual sulphur compounds invariably came from 1 to 3 per cent too low, how-

ever long they were fractioned, until they were a second time converted into the mercuric chloride compound and again separated by hydrogen sulphide. Upon diluting a second time, usually another portion of the sulphur-free oil collected, or remained in suspension and, after sufficient fractioning, the percentage of sulphur then corresponded to the value theoretically required.

It has already been explained that the vacuum fractions of the crude sulphur oil, before the separation of its constituents, is a mixture of an unsaturated hydrocarbon, a sulphur compound and another hydrocarbon of a series not determined. More attention will be given later to the sulphur-free oils. All the portions selected for the separation of these constituents had previously been fractionated from 4 to 20 times, for the most part *in vacuo*, and since the sulphur oil from any particular fraction has corresponded in boiling point to that of the fraction before separation, it has been possible to select, from the great number of first fractions, those which should give the bodies desired, thereby saving much time and unnecessary labor in searching for the individual constituents.

After the second precipitation from the mercuric chloride compound, a few distillations *in vacuo*, with the aid of a bead column, in a long-necked flask, have been sufficient to bring together, for the most part within 1° or 2°, the sulphur compound desired. For the separation without decomposition of the sulphur oils boiling above 130°, distillation *in vacuo* has been indispensable. Doubtless exclusion of air, as well as the reduction in boiling points, especially of the higher members, is essential.

The most volatile vacuum distillates, 40°–50°, were subjected to 8 additional distillations within limits of 2°, and 300 cc. of these distillates was agitated with an excess of alcoholic mercuric chloride. A part of the oil was immediately converted into a crystalline precipitate, and the sulphur-free oil, which formed the greater part of the oil taken, remained entirely in solution and was separated by dilution. After decantation of the alcoholic solution, the crystalline precipitate was well

washed with alcohol and light gasolin, and decomposed by hydrogen sulphide in presence of alcohol.

For complete removal of the sulphur-free oil the mercuric chloride compound was again formed, washed and the sulphur oil separated by hydrogen sulphide. Unfortunately, the larger portion of the sulphur oil was accidentally lost, but the remainder was fractioned, so far as possible, until, finally, it showed a tendency to collect at 125°–130°.

The percentage of sulphur found in this product was 27.12; required for the sulphur compound, $C_6H_{12}S$, 27.60. The crystalline condition of this substance is characteristic of the alkyl sulphides; but all the sulphur bodies we have separated from petroleum are viscous oils that could not be solidified, except the more volatile sulphur compounds such as were separated from Ohio petroleum, which were crystalline.

The following series of sulphur compounds, which have been identified by analysis and shown to have the composition of the general formula $C_nH_{2n}S$, do not represent any series known. They are not members of the ethylene sulphide series, as shown by their reactions and very high specific gravity. In empirical composition they correspond to hydrothiophenes, which have not been synthetically prepared.

Heptyl Thiophane.

Fraction 158°–160°, $C_7H_{14}S$.

The heptyl sulphur compound was identified in the vacuum distillate 71°–73° (50 mm.) seventh distillation. After precipitation with alcoholic mercuric chloride, and thorough washing with alcohol and light gasolin, the thick, viscous oil was decomposed with hydrogen sulphide, in the presence of alcohol. The oil that separated on dilution of the alcohol was fractionated *in vacuo* until it distilled at 74°–76° (50 mm.) and at 158°–160° (750 mm.). A determination of its sp. gr. at 20° gave 0.8878. Analysis gave percentages of carbon, hydrogen and sulphur required for the formula $C_7H_{14}S$. Carbon and hydrogen were determined by combustion in lead chromate, the sulphur by combustion in oxygen.

I. 0.1749 gram oil gave 0.4141 gram CO_2 and 0.1748 gram H_2O.

II. 0.1666 gram oil gave 0.3071 gram BaO_4.

	Calculated for $C_7H_{14}S$.	Found. I.	II.
C	64.63	64.59	. .
H	10.76	11.18	. .
S	24.61	. .	25.31

Octyl Thiophane.

Fraction 167°–169°, $C_8H_{16}S$.

For the separation of the next sulphur homologue the large quantity of distillate was selected that collected at 79°–81° (50 mm.) after the seventh distillation. One hundred cc., with the treatment described above, yielded 20 cc. of the sulphur compound, that distilled constant at 81°–83° (50 mm.) and at 167°–169° under atmospheric pressure. The sp. gr. of this oil was found to be 0.8929 at 20°. Analyses:

I. 0.1666 gram oil gave 0.4057 gram CO_2 and 0.1671 gram H_2O.

II. 0.1391 gram oil gave 0.2282 gram $BaSO_4$.

	Calculated for $C_8H_{16}S$.	Found. I.	II.
C	66.67	66.46	. .
H	11.11	11.22	. .
S	22.22	. .	22.53

Isooctyl Thiophane.

Fraction 183°–185°, $C_8H_{16}S$.

A large amount of distillate collected at 97°–99° (50 mm.), at the end of the seventh distillation, that gave, by analysis, the same empirical formula as the sulphur compound previously described. The term isooctyl is applied to this compound to distinguish it from its isomer. Upon treatment with mercuric chloride and second precipitation, a large amount of sulphur-free oil collected on dilution of the alcohol, and analysis showed that this constituent was completely removed by the second treatment. After fractionating *in vacuo* this product collected to the extent of 15 cc. at 94°–96° (50 mm.), and dis-

tilled, with some decomposition, at 183°–185°, atmospheric pressure. Sp. gr. at 20°, 0.8937. Analyses:

I. 0.1458 gram oil gave 0.3592 gram CO_2 and 0.1470 gram H_2O.

II. 0.1561 gram oil gave 0.3814 gram CO_2 and 0.1575 gram H_2O.

III. 0.2670 gram oil gave 0.4183 gram $BaSO_4$.

	Calculated for $C_8H_{18}S$.	Found. I.	II.	III.
C	66.67	67.19	66.16	. .
H	11.11	11.27	11.29	. .
S	22.22	. .	. .	21.52

It will be observed that the last two compounds have the same empirical composition, but differ by 16° or more in boiling points, and differ also in specific gravity. It will also be observed that they agree closely in boiling points with butyl and isobutyl sulphides; but they differ widely from the latter in specific gravity: butyl sulphide, 0.8523 at 0°; isobutyl sulphide, 0.8363 at 10°, and in other properties.

Nonyl Thiophane.

Fraction 139°–195° $C_9H_{18}S$.

A portion of the distillate that collected in considerable quantity at 106°–108° (50 mm.) was treated in the same manner as previously described, with two precipitations for the separation of the sulphur compound. The product was fractionated *in vacuo* until it collected, for the most part, at 106°–108° (50 mm.). Under atmospheric pressure it boiled at 193°–195°, and gave, as its sp. gr. at 20°, 0.8997. Analyses:

I. 0.1927 gram oil gave 0.4852 gram CO_2 and 0.2033 gram H_2O.

II. 0.1547 gram oil gave 0.2210 gram $BaSO_4$.

	Calculated for $C_9H_{18}S$.	Found. I.	II.
C	68.35	68.68	. .
H	11.40	11.80	. .
S	20.25	. .	19.62

Decyl Thiophane.

Fraction 207°–209°, $C_{10}H_{20}S$.

From the vacuum distillate, 114°–115° (50 mm.) after the seventh distillation, a sulphur oil was prepared by two precipitations with mercuric chloride, that collected, after fractioning some time *in vacuo*, for the most part, at 114°–116° (50 mm.). It distilled at 207°–209° (750 mm.) and gave sp. gr., at 20°, 0.9074. Analyses:

I. 0.2323 gram oil gave 0.5904 gram CO_2 and 0.2453 gram H_2O.

II. 0.1981 gram oil gave 0.5078 gram CO_2 and 0.2094 gram H_2O.

III. 0.1654 gram oil gave 0.2240 gram $BaSO_4$.

IV. 0.1760 gram oil gave 0.2407 gram $BaSO_4$.

	Calculated for $C_{10}H_{20}S$.	Found. I.	II.	III.	IV.
C	69.77	69.33	69.92	. .	. .
H	11.62	11.32	11.82	. .	. .
S	18.60	. .	. .	18.59	18.78

Undecyl Thiophane.

Fraction 128°–130° (50 mm.), $C_{11}H_{22}S$.

The vacuum distillate, 135°–145° (50 mm.), was selected for the separation of the next homologous sulphur compound. A thick, tarry mass was formed by precipitation with mercuric chloride, which gave the pure sulphur oil by a second precipitation. The viscosity of the compounds with mercuric chloride was found to increase with increase in molecular weights of the sulphur oils. Three hundred grams of the first distillate, 135°–145°, fourth distillation, gave, after the second precipitation with mercuric chloride, 122 grams insoluble in alcohol, 60 grams in the alcoholic solution, and 84 grams of the sulphur oil. Without further purification, the latter gave 16.08 per cent sulphur. After continued fractioning *in vacuo* the sulphur oil collected, for the most part, at 128°–130° (50 mm.). Analyses:

I. 0.1793 gram oil gave 0.4669 gram CO_2 and 0.1896 gram H_2O.

II. 0.2064 gram oil gave 0.5334 gram CO_2 and 0.2122 gram H_2O.

III. 0.1921 gram oil gave 0.2411 gram $BaSO_4$.

	Calculated for $C_{11}H_{22}S$.	Found. I.	II.	III.
C	70.98	71.01	70.71	. .
H	11.82	11.82	11.50	. .
S	17.20	. .	. .	17.24

The sp. gr. of this sulphur oil was found to be 0.9147, at 20°. Particular attention was given to the purification of this product, to be certain of the series as shown by the most careful analysis. In addition to the determinations given above that demonstrate its composition, the following additional analyses were made of different preparations: carbon found, 70.73, 70.74; hydrogen in the same combustions, 11.48, 11.95; sulphur, 17.28, 17.05, 17.10.

The portions of the original sludge oil, called sulphur-free oils to distinguish them from the sulphur oils, have contained from 0.1 to 0.3 per cent of sulphur, and it has been assumed that the small proportion of sulphur indicated a little of the sulphur compound not precipitated by mercuric chloride. That the part collecting above the alcohol, after precipitation, is a different product from the part remaining in solution in alcohol is shown by the difference in specific gravity. For example, the distillate 136°–145°, from which the oil $C_{11}H_{22}S$ was obtained, gave an oil insoluble in alcohol with sp. gr. 0.8412; but the sp. gr. of the portion in solution was found to be 0.8107. Similar differences appeared in oils associated with other thiophanes. Since the specific gravity of any one of the principal hydrocarbons in Canadian petroleum corresponding in boiling point with these bodies is smaller than the specific gravity of the sulphur oils, and since hydrocarbons are sparingly soluble in sulphuric acid and alcohol, the bodies under examination cannot be the principal petroleum hydrocarbons. Then the odors of both the substances soluble and insoluble in alcohol are unlike that of any of the hydrocarbons—very pungent, resembling the terpenes. Further study will be necessary to identify these peculiar bodies.

Quatdecyl Thiophane.

Fraction 266°–268°, $C_{14}H_{28}S$.

This sulphur oil was separated from the distillate 160°–170° (50 mm.), fourth distillation. After the second precipitation and decomposition by hydrogen sulphide, 400 grams of the sludge distillate gave 75 cc. of a yellow oil that collected, for the greater part, at 168°–170° (50 mm.), after extended fractioning. It collected at 266°–268° (750 mm.). Its sp. gr. at 20° was found to be 0.9208. Analyses:

I. 0.1859 gram oil gave 0.5010 gram CO_2 and 0.2109 gram H_2O.

II. 0.2290 gram oil gave 0.2336 gram $BaSO_4$.

	Calculated for $C_{14}H_{28}S$.	Found. I.	II.
C	73.68	73.52	. .
H	12.28	12.69	. .
S	14.04	. .	14.02

Sexdecyl Thiophane.

Fraction 283°–285°, $C_{16}H_{32}S$.

From 400 cc. of the first vacuum distillate 170°–180° (50 mm.), after the second precipitation with mercuric chloride and long-continued distillation, 28.5 grams of the sulphur oil collected at 184°–186°, which distilled, with some decomposition, at 283°–285° (750 mm.). Its sp. gr. was found to be 0.9222. Analyses:

I. 0.2148 gram oil gave 0.5934 gram CO_2 and 0.2380 gram H_2O.

II. 0.1850 gram oil gave 0.1683 gram $BaSO_4$.

	Calculated for $C_{16}H_{32}S$.	Found. I.	II.
C	75.00	75.36	. .
H	12.50	12.40	.
S	12.50	. .	12.49

Octodecyl Thiophane.

Fraction 290°–295°, $C_{18}H_{36}S$.

From 350 grams of the vacuum distillate 191°–210° (50

mm.), alcoholic mercuric chloride gave a very thick, viscous precipitate, from which was obtained, after the second precipitation, 50 grams of a dark colored oil that collected, after continued distillation *in vacuo*, nearly colorless, for the most part, at 198°–202°. Under atmospheric pressure this oil distilled, with some decomposition, at 290°–295°; sp. gr., at 20°, 0.9235. The values obtained by analysis corresponded to the formula $C_{15}H_{30}S$.

I. 0.2005 gram oil gave 0.5602 gram CO_2 and 0.2214 gram H_2O.

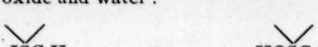
II. 0.1937 gram oil gave 0.1634 gram $BaSO_4$.

III. 0.2011 gram oil gave 0.1636 gram $BaSO_4$.

	Calculated for $C_{15}H_{30}S$.	Found. I.	II.	III.
C	76.06	76.22	. .	
H	12.67	12.35	. .	. .
S	11.27	. .	11.57	11.18

We have made no attempts toward the separation of sulphur compounds with higher molecular weights, but there is no doubt that higher homologues are contained in the less volatile distillates which we have separated from the original oil. It is probable that intermediary members of this series are contained in the distillates examined, and that they might be identified in larger quantities of material.

As has been shown in the method of preparation, the thiophanes combine readily with alcoholic mercuric chloride to form viscous oils. They also form addition products with chlorplatinic acid, which are heavy, viscous oils. When heated in a sealed tube with ethyl iodide, addition products are formed which crystallize in small prisms,—$C_nH_{2n}S$, C_2H_5I.—These addition products form alkaline hydroxides when warmed with silver oxide and water :



Bromine exerts a characteristic action on these sulphur compounds. Immediately, when they come in contact, combination follows with almost explosive violence, and copious evolu-

tion of hydrobromic acid, in equivalent amounts to the bromine added. It is wholly unlike the behavior of unsaturated hydrocarbons with bromine. Probably part of the bromine combines with the sulphur, but the evolution of hydrobromic acid begins immediately, doubtless due to the ready replacement of the methylene hydrogen atoms.

The thiophanes still further resemble the well-known series of sulphur derivatives in their behavior toward oxidation. The formation and properties of the sulphones will be described later.

In addition to the analytical data that establish the composition of the thiophanes, we have determined their indices of refraction, and the corresponding molecular refraction verifies the formulas given by analysis.

Indices of Refraction of the Thiophanes.

Many attempts were made, with different solvents, to determine the molecular weights of the sulphur compounds in Canadian petroleum, but no concordant values could be obtained, even with the same substance and the same solvent.

Better success, however, was reached in ascertaining the indices of refraction, but since the values for sulphur in organic compounds have not been determined with the same certainty as in the case of carbon, hydrogen and oxygen, some attention was given to verifying this constant.

The index of refraction found by Nasini for ethyl sulphide was 1.44233; for ethyl mercaptan, 1.43055; and for ethyl disulphide, 1.50633.

Assigning the accepted values to carbon and hydrogen, the calculated value for sulphur becomes, for ethyl sulphide, 7.98; for ethyl mercaptan, 7.81; and for ethyl sulphide, 8.03. In determining the value of sulphur in ethyl mercaptan, we found the angle to be 49° 24′, which corresponds to the index 1.4323, and the calculated value for sulphur is 7.89.

Isobutyl sulphide gave us 1.4585 as its index of refraction, calculated from the observed angle 44° 57′; the corresponding molecular refraction is 46.85. Assigning the accepted values to carbon and hydrogen, the difference is the value of sulphur,

7.98, the same as the value calculated from Nasini's index of ethyl sulphide.

The index assigned to thiophen is 1.5268, which gives as its molecular refraction, 24.12, leaving a value for sulphur 6.53. Thiophen is assumed to have two sets of double bonds. The petroleum sulphur compounds under consideration, although doubtless possessing a ring structure, apparently do not contain carbon atoms connected by double linkage. We have, therefore, considered it safe to use the value 7.98 for sulphur, and the following molecular refraction for the petroleum sulphur compounds were calculated on the basis of this value:

Heptyl Thiophane.

The fraction 74°–76° (50 mm.), which proved to contain heptyl thiophane, gave as its index of refraction 1.468, corresponding to the following molecular refraction:

Calculated for $C_7H_{14}S$.	Found.
40.15	40.82

Octyl Thiophane.

From the fraction 83°–85° (50 mm.) was separated octyl thiophane. Its index of refraction was found to be 1.4860, and its molecular refraction:

Calculated for $C_8H_{16}S$.	Found.
44.75	44.91

Nonyl Thiophane.

Nonyl thiophane was found to be the principal constituent of the fraction 106°–108° (50 mm.). It gave, as its index of refraction, 1.4746, from which was calculated its molecular refraction:

Calculated for $C_9H_{18}S$.	Found.
49.35	49.50

Decyl Thiophane,
$C_{10}H_{20}S$.

The index of refraction of the distillate 114°–116°, from

which was separated decyl thiophane, we found to be 1.4766. Its molecular refraction was calculated as follows :

Calculated for $C_{10}H_{20}S$.	Found.
53.94	53.60

Undecyl Thiophane.

Undecyl thiophane was found in the fraction 130°–135° (50 mm.). We found its index of refraction to be 1.480, and its molecular refraction :

Calculated for $C_{11}H_{22}S$.	Found.
58.54	58.53

Quatdecyl Thiophane.

$C_{14}H_{28}S$.

The fraction 168°–170° gave quatdecyl thiophane. Its index of refraction, 1.4892, corresponded to the molecular refraction :

Calculated for $C_{14}H_{28}S$.	Found.
72.33	71.61

Sexdecyl Thiophane.

This sulphur compound was found in the fraction 184°–186° (50 mm.). Its index of refraction proved to be 1.4903, from which its molecular refraction was calculated :

Calculated for $C_{16}H_{32}S$.	Found.
81.52	80.44

The index of refraction of octodecyl thiophane was found to be 1.4977, but the molecular refraction calculated from this value and its sp. gr. 0.9625 at 20°, gave a value different by 4 units from the calculated molecular refraction.

Oxidation Products of the Thiophanes.

Appreciating the importance of oxidation products in ascertaining the composition of the thiophanes, we have tried very thoroughly the action of oxidation agents, nitric acid, chromic acid and potassium permanganate. These sulphur compounds

absorb oxygen with great readiness, and the reaction must be carefully controlled to prevent ultimate oxidation to sulphuric acid. It was not found possible to limit the oxidation to the formation of the sulphoxide, since the sulphone seems to be the more stable condition. Nitric acid readily oxidizes the sulphur with an extremely violent reaction, but, apparently, also forms nitro derivatives, since the products contain nitrogen.

Chromic acid oxidizes the sulphur readily, with some danger that the reaction proceeds to ultimate oxidation. Potassium permanganate, in either alkaline or acid solution, readily effects the change with little danger of the formation of sulphuric acid. After careful study of the conditions, it was found that the largest yield of oxidation product was obtained by adding slowly, to the oil, 1.5 times the calculated weight of permanganate, dissolved in 30 times its weight of water, keeping the solution cold. With efficient cooling, the permanganate can be added as rapidly as it is decolorized. After the reaction was complete the precipitated manganic oxide was filtered and the solution distilled with steam, which carried over any unoxidized sulphur compound, leaving behind the oxidation product. When carefully conducted, the solution shows no sulphuric acid. From the residue of the steam distillation the oxidation product was extracted with ether and the ether evaporated, leaving a thick, heavy oil, which increased in viscosity with increase in molecular weight. In several instances we dissolved the precipitated manganic oxide by saturating with sulphurous oxide and extracted with ether. When the oxidation is complete this is the easier method ; but distillation with steam insures the removal of any decomposition products.

The action of oxidizing agents showed a wide difference in deportment between the sulphur compounds from Canadian petroleum and sulphides synthetically prepared. For example, synthetic isoamylsulphide, allowed to stand with concentrated nitric acid, showed vigorous reaction only after several minutes, with evolution of heat. After the reaction ceased heat was applied and water added. The oxidation product

collected above the water and partly dissolved. Only a trace of sulphuric acid was found in the solution. On treating the sulphur compounds from Canadian petroleum in the same manner, the reaction was much more vigorous, with immediate evolution of heat. The product formed a thick oil, heavier than water, and much sulphuric acid was formed, but the oxidized oil contained much sulphur, showing that it consisted, in part, of an oxidized sulphur compound. This difference in the action of nitric acid is pretty conclusive proof that the sulphur compounds under consideration are not alkyl sulphides, nor, indeed, members of any other well-known series. It is in accordance with the observation that the hydro-ring compounds, the methylenes, are less stable toward reagents than the aromatic or paraffin compounds.

Hexyl Thiophane Sulphone.

The presence of hexyl thiophane was indicated in the fraction 125°–130° (atmospheric pressure), although it was not separated in a pure form. In attempting to prepare the sulphone, the fraction 55°–57° (50 mm.) was treated, as described above, with potassium permanganate. Oxidation was rapid, even when cooled to 0°. In this instance, after dissolving the manganic oxide in sulphurous acid, the solution was evaporated to dryness and the residue extracted with anhydrous ether. Evaporation of the ether left a thick, viscous oil with a sweetish taste and odor, with no reaction for sulphuric acid. While the analytical values obtained indicated that the hexyl compound was contaminated with a higher homologue, it is evident that hexyl thiophane was the principal constituent. Analysis:

C, 49.39; H, 8.47; S, 19.02. Required for $C_6H_{12}SO_2$: C, 48.64; H, 8.11; S, 21.62.

Heptyl Thiophane Sulphone,
$C_7H_{14}SO_2$.

The oxidation of heptyl thiophane was conducted as described above. After neutralizing with sodium carbonate and evaporating to dryness, the residue was extracted with anhy-

drous ether. No sulphuric acid was formed by the oxidation. Analysis :

I. 0.1992 gram substance gave 0.3801 gram CO_2 and 0.1531 gram H_2O.

II. 0.1628 gram substance gave 0.2279 gram $BaSO_4$.

	Calculated for $C_7H_{14}SO_2$.	Found. I.	II.
C	51.86	52.05	. .
H	8.64	8.59	. .
S	19.75	. .	19.23

This sulphone formed a very thick, heavy oil. Its sp. gr. was found to be 1.1138 at 20°.

Octyl Thiophane Sulphone,
$C_8H_{16}SO_2$.

Fifty grams of the fraction 87°–89°, identified as octyl thiophane, was oxidized carefully at 0°. After dissolving the manganic oxide and distilling with steam, 36 grams of a heavy oil separated, with no formation of sulphuric acid. After neutralizing with sodium carbonate, evaporating to dryness and extracting with ether, this oil gave, as its sp. gr. at 20°, 1.1142. Analysis :

I. 0.1697 gram substance gave 0.3385 gram CO_2 and 0.1368 gram H_2O.

II. 0.2038 gram substance gave 0.2702 gram $BaSO_4$.

	Calculated for $C_8H_{16}SO_2$.	Found. I.	II.
C	54.55	54.41	. .
H	9.11	9.01	. .
S	18.18	. .	18.21

Nonyl Thiophane Sulphone,
$C_9H_{18}SO_2$.

For oxidation of the nonyl sulphur compound, the fraction 106°–108° (50 mm.) was selected. In the first half of the oxidation the potassium permanganate was added slowly, in a bath of ice and salt. The reaction was completed at ordinary temperatures, and it proceeded much more slowly toward the end. The required amount of permanganate was consumed in

4 days, and no sulphuric acid was formed. In all these oxidations doubtless sulphonic acids were formed to some extent, but their removal was insured by neutralizing with sodium hydroxide and extraction of the evaporated residue with anhydrous ether. The sp. gr. of the nonyl sulphone was found to be 1.1161, at 20°. Analysis:

I. 0.1867 gram substance gave 0.3874 gram CO_2 and 0.1509 gram H_2O.

II. 0.1679 gram substance gave 0.2071 gram $BaSO_4$.

	Calculated for $C_9H_{18}SO_2$.	Found. I.	II.
C	56.83	56.61	. .
H	9.47	9.04	. .
S	16.84	. .	16.93

Undecyl Thiophane Sulphone,
$C_{11}H_{22}SO_2$.

We were unable to isolate an oxidation product which corresponded closely in composition to decyl thiophane sulphone from the original fraction, and the amount of the thiophane isolated was not sufficient for oxidation.

Undecyl thiophane sulphone was prepared from the undecyl thiophane, separated from the fraction 129°–131° (50 mm.); 7.8 grams of the thiophane gave 5 grams of the oxidation product. The heavy oil, left after distillation with steam, had a pleasant, sweetish odor; its sp. gr. was found to be 1.1126, at 20°. Analysis:

I. 0.1903 gram substance gave 0.4176 gram CO_2 and 0.1621 gram H_2O.

II. 0.1470 gram substance gave 0.1579 gram $BaSO_4$.

	Calculated for $C_{11}H_{22}SO_2$.	Found. I.	II.
C	60.54	59.84	. .
H	10.09	9.53	. .
S	14.68	. .	14.75

Dodecyl Thiophane Sulphone,
$C_{12}H_{24}SO_2$.

After treating 7 grams of the distillate 142°–144° (50 mm.)

with 9 grams of potassium permanganate, the proportions found most suitable, there still remained a slight odor of the thiophane, which was completely removed by distillation with steam. The oil that remained after extraction of the steam residue with ether gave, as its sp. gr. at 20°, 1.1372. Analysis :

I. 0.1533 gram substance gave 0.3483 gram CO_2 and 0.1402 gram H_2O.

II. 0.1645 gram substance gave 0.1554 gram $BaSO_4$.

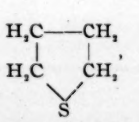
	Calculated for $C_{12}H_{24}SO_2$.	Found. I.	Found. II.
C	62.07	61.98	. .
H	10.35	10.23	. .
S	13.79	. .	12.91

The sulphur compounds in Canadian petroleum have been shown to belong to a series C_nH_{2n}. Their structure must be explained either as unsaturated, like the ethylene sulphides, or by a ring arrangement. That these bodies are not of the ethylene series is shown by the facts that the ethylene sulphides are solids, and that they absorb bromine without evolution of hydrobromic acid. The petroleum sulphur compounds have a very high specific gravity, and they evolve hydrobromic acid copiously when treated with bromine. They resemble the well-known series of sulphur compounds in forming addition products with mercuric chloride, in the formation of sulphones, the formation of addition products with alkyl iodides and alkaline hydroxides.

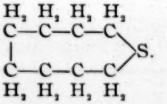
In a former paper by Mabery and Smith it was shown that the sulphur compounds in petroleum are not mercaptans nor thiophens. The series separated by Mabery and Smith from Ohio petroleum formed crystalline addition products with alcoholic mercuric chloride, and the sulphur oils themselves resembled the alkyl sulphides. But the series contained in the portions of Canadian petroleum with higher boiling points are not alkyl sulphides, mercaptans, thiophens, nor ethylene sulphides. Their high specific gravity shows that they belong to a new series. The cyclic condition of the constituents of

Pennsylvania, Ohio, Canadian, Texas and California petroleum corresponding to the series C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, etc., has been described in former papers, and the proportions of these series are indicated by the differences in specific gravity. Canadian petroleum is composed, for the most part, of the series of hydrocarbons poorer in hydrogen. Other constituents of petroleum partake of a similar cyclic condition. The nitrogen compounds, for example, in California petroleum, are tetrahydro and octohydro bodies, with a structure resembling that of the hydroquinolines.

Empirically, the thiophanes are hydrothiophens with long side chains, methylene sulphides with numerous or long side chains, or simple ring methylene sulphides. Either class of formulas will satisfy the results of analysis. For example:

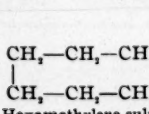


Tetrahydrothiophene or pentamethylene sulphide.

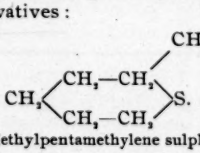


The ready formation of sulphones, addition products with alkyl iodides and hydrates, is unlike the thiophens, but the hydrothiophens may behave differently. It is improbable that rings with a very large number of carbon atoms can exist. A condensed ring structure like quinoline or naphthoquinoline, with sulphur in place of nitrogen, is excluded by the series C_nH_{2n}.

As shown above, the lowest member of the series separated from Canadian petroleum was $C_6H_{12}S$, boiling point 45°–50° (50 mm.), which may be hexamethylene sulphide, or methylpentamethylenesulphide. Higher homologues may reasonably be considered as side chain derivatives:



Hexamethylene sulphide.



Methylpentamethylene sulphide.

The structure of these bodies will doubtless have to be referred to the methylene ring, yet the precise form of the ring with reference to the number of carbon atoms it contains is still uncertain. For instance, the central group may be a penta, hexa, or heptamethylene ring. It has, therefore, seemed advisable to employ a comprehensive name that shall include any possible arrangement, and the term thiophane has been adopted. Without doubt, the structure of these sulphur derivatives will be defined with greater precision when the structure of the hydrocarbons of the series C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, etc., which constitute the greater part of the constituents of petroleum with high boiling points from any source, are better understood.

Unsaturated Hydrocarbons of the Series C_nH_{2n}.

The need of more accurate information concerning the presence of hydrocarbons of the ethylene series, C_nH_{2n}, in petroleum, was explained in a former paper of this series. Notwithstanding persistent attempts in the numerous treatises on petroleum to show that these bodies have been identified, a critical examination of published results fails to reveal adequate proof of sufficient foundation for these statements. The statement in "Petroleum and Its Products," by Redwood, that De la Rue and Mueller proved the presence, in preponderating quantities, of the ethylene group in Rangoon petroleum is not supported by the results, nor by the conclusions of those authors. Concerning the results of Warren, Schorlemmer and Chandler, it is not true, as asserted by Redwood, that those chemists found the ethylene series in Pennsylvania petroleum. There are no allusions to this series in Schorlemmer's published papers.

Beyond adopting the general nomenclature then accepted for the ethylene series, Warren evidently left it an open question as to what should be the structural formulæ of the products he separated from Pennsylvania petroleum. There are no statements in his papers to show that he made any further preparation of his products for analysis than boiling with sodium, and no further examination to prove structural forms.

Certainly it would have been easy to demonstrate the unsaturated condition of those bodies had they contained doubly bonded carbon, and in view of Warren's clear-sighted and painstaking methods, he could not have overlooked the importance of those tests. In none of his papers on Pennsylvania petroleum does the term olefine or ethylene appear.

The assertion of Hoefer that members of the olefine series, C_2H_4 to $C_{30}H_{60}$, have been found in American petroleum, has no foundation. In fact, besides the investigations within recent years in this laboratory leading to a better knowledge of the various series of hydrocarbons with high boiling points, no attempts have been made to discover the true composition of American petroleum. In fractions below 200° from Galician oil, Lachowicz obtained no reaction with bromine, yet, so far as they have been examined in this laboratory, distillates below 200° from American oils do not fail to show a considerable bromine absorption. The sulphur compounds in Ohio and Canadian oils have a great affinity for bromine. Substitution may take place in the aromatic hydrocarbons which American oils contain, as well as in the hydrocarbons C_nH_{2n+2}, unless light is excluded. All these bodies, and probably others, are affected in the ordinary determinations of bromine absorption.

At the suggestion of one of us (C. F. M.), in connection with another line of work on petroleum, Mr. T. A. Hicks, a student in this laboratory, undertook a study of bromine absorption in crude oil and in fractions obtained from it after various modes of treatment. Two determinations in the oil before treatment gave, as the percentage of bromine absorbed, (I.) 8.43 and (II.) 8.73. A portion agitated with alcoholic mercuric chloride, washed and dried, gave (I.) 9.27 and (II.) 9.58, indicating that the crude oil holds in solution, to some extent, the mercuric chloride compound. After treatment with mercuric chloride, a portion of the oil shaken with common concentrated sulphuric acid gave with bromine, (I.) 5.91 and (II.) 5.94. The oil was next shaken with fuming sulphuric acid, washed and dried, when it absorbed bromine equivalent to (I.) 3.47 and (II.) 3.72. A portion of the oil, after the last treatment, was distilled under atmospheric pres-

sure, fractions collected at 100°–125°, 125°–200°, and 200°–230°. In the first distillate the bromine absorption was, (I.) 4.65, (II.) 4.75; in the second (I.) 4.63, (II.) 4.58; and in the third (I.) 5.61, (II.) 5.17 per cent. Another portion of the treated oil was distilled under 50 mm., collecting at 130°–160°, 160°–190°, 190°–260°, and a residue, and the bromine absorption determined. Bromine absorption gave in the first distillate (I.) 1.73, (II.) 2.00; in the second (I.) 1.96, (II.) 2.01; in the third (I.) 3.28, (II.) 3.15; and in the residue 9.52. From these results it is evident that substitution in the less volatile portions of the crude oil or cracking has much to do with the amount of bromine absorbed, especially since, in these experiments, the reagents employed for the removal of the sulphur compounds should also remove unsaturated hydrocarbons. In this connection Mr. Hicks determined bromine absorption in some distillates from Pennsylvania, Ohio and Canadian oils, that has been especially purified by long distillation and treatment with reagents, as has been more fully described in another paper. A distillate, 194°–196°, from Pennsylvania petroleum, gave 0.02 per cent bromine absorbed; another, 209°–210°, 0.09 per cent; a distillate, 209°–210° Ohio, purified in the same manner, gave 0.03 per cent bromine, and a Canadian distillate, 0.12 per cent. These results may be accepted as showing no absorption of bromine, since this method is not capable of indicating such small percentages. That the quantity of sulphur remaining in the crude oil, after treating with fuming sulphuric acid, was too small to affect the amount of bromine absorbed, is shown by the low percentage of sulphur, 0.09 and in the distillate 200°–230°, atmospheric pressure, 0.001 per cent.

When the complex composition of American petroleum is borne in mind, and the probability of substitution in the less volatile portions, the difficulties in testing for unsaturated hydrocarbons are evident. Consequently, all discussion of this subject by those best informed has been undertaken with reservation, while those of others partake more of the nature of speculation on results which the authors were content merely

with presenting, without attempting explanations which the facts were insufficient to justify.

We have had good evidence that unsaturated hydrocarbons are contained in distillates prepared from crude petroleum. Polymerization on standing, the formation of dark colored, heavy oils can only be explained by changes in unsaturated hydrocarbons or unsaturated sulphides. Heptylene was described in another paper as a constituent of Ohio oil.

Since the products described in this paper were contained in the oil extracted with sulphuric acid from burning oil distillate, we have assured ourselves, by experiments already described, that ordinary concentrated sulphuric acid, such as is used in refining burning oil distillates, removes from such distillates, without decomposition, the unsaturated hydrocarbons as well as the sulphur compounds, and, consequently, that the sludge oil, after carefully separating from the acid, contained constituents of the crude oil and not products of decomposition.

In fractioning *in vacuo*, as previously explained, a considerable proportion of the distillates from the sludge oil collected below 100°, which could be distilled without decomposition under atmospheric pressure. These portions were, therefore, carried through 10 distillations under atmospheric pressure, and the portions distilling below 150° *in vacuo* also through 10 additional separations *in vacuo*. On account of great pressure of other work, these distillates stood 3 years before their study was resumed, although, when first obtained, they received sufficient attention to show that they contained unsaturated hydrocarbons.[1]

Upon returning to these distillates, it was found that some of them had undergone a marked change. Those collected at certain temperatures—especially at 44°–45°, seventh distillation (50 mm.); 70°–71°, twenty-second distillation (atmospheric pressure); 97°–98°, tenth distillation (atmospheric pressure); 118°–119°, tenth distillation (atmospheric pressure)—corresponding, in part, to the boiling-points of well-known hydrocarbons of the ethylene series, C_nH_{2n}, had deposited

[1] THIS JOURNAL, 16, 92.

heavy, dark red oils in considerable quantities, evidently products of polymerization. Some of the polymerized oils were found to contain as much as 8 per cent of sulphur, although polymerization took place in oils containing not more than 1.5 per cent of sulphur. It was interesting to observe that distillates on either side of those from which the heavy oils separated remained unchanged and were scarcely more discolored than when they were first distilled. That the distillates below 150° contain sulphur compounds with a peculiar odor, attacking the eyes, and in other respects different from the series $C_nH_{2n}S$ described above, has been apparent since the first distillation of these oils, although these peculiar compounds are evidently present in much smaller proportions than the others.

All these fractions, as well as those above 150°, united with bromine with explosive violence, and with the evolution of great heat. The bromine addition products, however, were found to be so unstable that it was impossible to purify them by distillation even *in vacuo*. They decomposed rapidly, even on standing, with the separation of hydrobromic acid. In ascertaining the composition of these hydrocarbons we have, therefore, relied on the more stable addition product obtained with hydrobromic acid, which had the further advantage that, having no action on the sulphur compounds, the latter need not be removed before heating with the acid.

Hexylene.

For the identification of hexylene, the small quantity of the fractions 70°–80°, twenty-second distillation (atmospheric pressure), were put together, and a portion was heated to 120°, during 5 hours, with fuming hydrobromic acid. The product was washed, dried and fractionated *in vacuo*. On account of the higher boiling point of the bromide it was easy to separate the addition product and, of the small quantity obtained, the greater portion collected at 62°–65° (50 mm.). The boiling point of the bromide under atmospheric pressure could not be determined on account of its instability, but it probably was not far from 135°. The distillate selected for the formation of this bromide was nearly the same in boiling point as that of

the hexylenes from various sources, 65°–70°. Upon analysis values were obtained corresponding to those required for monobromhexane:

I. 0.1938 gram oil gave 0.3108 gram CO_2 and 0.1283 gram H_2O.

II. 0.2720 gram oil gave 0.3045 gram AgBr.

	Calculated for $C_6H_{13}Br$.	Found. I.	II.
C	43.63	48.73	. .
H	7.88	7.41	. .
Br	48.51	. .	47.64

On account of the small amount of this substance it was not possible to purify it more completely.

Heptylene.

The fractions 98°–102°, tenth distillation (atmospheric pressure), more nearly corresponding to the boiling points of the various heptylenes, 90°–100°, were selected especially because they contained a considerable quantity of the polymerized oil. On either side of these limits the distillates had not changed. After treatment with fuming hydrobromic acid and fractioning *in vacuo*, the greater portion of the bromide collected at 76°–80° (50 mm.). It could not be distilled under atmospheric pressure, but its boiling point was probably not far from 160°. The results of analysis corresponded to the composition of monobromheptane:

I. 0.2000 gram oil gave 0.3498 gram CO_2 and 0.1592 gram H_2O.

II. 0.2117 gram oil gave 0.2188 gram AgBr.

	Calculated for $C_7H_{15}Br$.	Found. I.	II.
C	46.97	47.71	. .
H	8.38	8.90	. .
Br	44.73	. .	43.99

The sp. gr. of this heptyl bromide was found to be 1.1601.

Octylene.

Octylene was sought for in the fraction 118°–119°, tenth distillation (atmospheric pressure), from which had separa-

ted a small quantity of the heavy polymerized oil. After heating with concentrated hydrobromic acid, the oil was fractioned *in vacuo* until 15 grams collected at 93°–95° (50 mm.), corresponding, approximately, to 180°, atmospheric pressure. The boiling point of the distillate selected is near that of diisopropyl ethylene, 116°–120°, and also that of the octylene, 115°–117°, prepared from octyl chloride by Schorlemmer.

Analyses of the bromide gave values required for monobromoctane:

I. 0.1941 gram oil gave 0.3486 gram CO_2 and 0.1613 gram H_2O.

II. 0.1885 gram oil gave 0.1851 gram AgBr.

	Calculated for $C_8H_{17}Br$.	Found. I.	II.
C	49.74	49.00	. .
H	8.81	9.23	. .
Br	41.45	. .	41.83

The sp. gr. of this octyl bromide was found to be 1.1836.

Nonylene.

The fraction 140°–141°, tenth distillation (atmospheric pressure) was selected for the addition of hydrobromic acid. In fractioning the bromide *in vacuo*, after the separation of the portion not affected by the acid, the temperature rapidly rose to 110°, and more of the distillate collected at 110°–113° than at any other point in this vicinity. This product was less stable than the lower homologues, but its boiling point under atmospheric pressure would probably be in the vicinity of 200°. Upon analysis it gave values required for bromnonane:

I. 0.1798 gram oil gave 0.3481 gram CO_2 and 0.1501 gram H_2O.

II. 0.2117 gram oil gave 0.1888 gram AgBr.

	Calculated for $C_9H_{19}Br$.	Found. I.	II.
C	52.17	52.80	. .
H	9.18	9.33	. .
Br	38.65	. .	37.96

The sp. gr. of this bromnonane was 1.2084.

Higher fractions failed to give us addition products with hydrobromic acid, either because the additive power of the hydrocarbon was too weak, or because, if the addition product were formed, it was decomposed by distillation *in vacuo*. The first explanation is probably correct, since we have never noticed the evolution of hydrobromic acid in any considerable quantity. Perhaps it is more reasonable to assume that our distillates contained no higher homologues of this series than those that were identified.

With reference to the solvent power of sulphuric acid for the hydrocarbons described above, it is doubtless true that compounds with this acid of the hydrocarbons with high molecular weights are less stable, and partake more of the nature of mechanical solution. It is, doubtless, also true that the mechanical solvent power of the acid is increased by the other oils that the acid dissolves. If the acid solution separated from the oil be neutralized with calcium hydroxide, certain lime salts are formed, crystallizing in long needles, and consisting, at least in part, of nitrogen bases, but sulphonates of the ethylene hydrocarbons and of allied series have not been observed. That unsaturated hydrocarbons may be extracted by sulphuric acid and precipitated by dilution, has been shown in several experiments. We diluted a carboy of sludge acid by pouring slowly into water, and found the precipitated oils to contain these hydrocarbons. As to their relative proportion in the crude oil we have no precise data, but in comparison with the principal constituents it is extremely small.

Since the sulphur compounds described in this paper, as well as the alkyl sulphides, are also readily soluble in sulphuric acid, they should be removed as a part of the sludge in refining burning oil distillates.

The results described in this paper may be summarized as follows: The separation from Canadian petroleum of the following series of sulphur compounds: hexyl, heptyl, octyl, nonyl, decyl, undecyl, quatdecyl, sexdecyl, octodecyl thiophanes; the formation of corresponding sulphones by oxidation.

Canadian petroleum contains, in minute proportions, un-

saturated hydrocarbons, C_nH_{2n}, apparently of the ethylene series. Canadian petroleum contains certain sulphur-free oils soluble in alcohol, and different in odor and in other respects from the series hitherto identified in petroleum, possibly terpenes.

We desire to acknowledge our obligations to Messrs. C. A. Lattimer and R. C. McBride for assistance in the purification and analysis of the sulphur compounds.

Contributions from the Sheffield Laboratory of Yale University.

CXXX.—THE RELATIVE SOLUBILITY OF SOME DIFFICULTLY SOLUBLE CALCIUM AND BARIUM SALTS.

By H. W. Foote and G. A. Menge.

It is well known that the readily soluble salts of calcium are, in general, more soluble than the corresponding barium salts. This is true, for instance, of the chlorides, bromides, iodides, nitrates and chlorates. Of the difficultly soluble salts calcium sulphate is, of course, more soluble than barium sulphate.

In the following investigation the attempt has been made to measure the relative solubility of

(*a*) Calcium and barium carbonates,
(*b*) Calcium and barium oxalates,
(*c*) Calcium and barium fluorides.

By the term "relative solubility" is meant the ratio of the solubility of each salt alone, in water, at a given temperature.

The method which we adopted consisted essentially in treating the difficultly soluble calcium salt with a solution of barium chloride of known concentration and the corresponding barium salt with an equivalent solution of calcium chloride. The mixtures were shaken until no further action occurred, as determined by analysis, and from the proportions of barium and calcium in the solution we hoped to be able to calculate the relative solubilities. This could not be done accurately in every case, as will be shown.

Calcium and Barium Carbonates.

In a saturated solution of calcium carbonate alone, or of barium carbonate alone, the following expressions would hold in case hydrolysis were absent:

$$Ca \times CO_3 = K_1 \quad (1);$$
$$Ba \times CO_3 = K_2 \quad (2).$$

The chemical symbols stand for the concentrations and K_1 and K_2 represent the solubility products[1] of calcium carbonate and barium carbonate, respectively.

Since in (1) $Ca \equiv CO_3$ and in (2) $Ba \equiv CO_3$, it follows that

$$Ca^2 = K_1 \quad (3),$$
$$Ba^2 = K_2 \quad (4),$$

and, as the amounts of calcium and barium are equivalent to calcium carbonate and barium carbonate,

$$Ca \equiv CaCO_3 = \sqrt{K_1} \quad (5);$$
$$Ba \equiv BaCO_3 = \sqrt{K_2} \quad (6).$$

Dividing (5) by (6),

$$\frac{CaCO_3}{BaCO_3} = \frac{\sqrt{K_1}}{\sqrt{K_2}} \quad (7).$$

That is, excluding hydrolysis, the relative solubility of calcium and barium carbonates is equal to the ratio of the square roots of their solubility products.

A saturated, aqueous solution of calcium or barium carbonate is, however, largely hydrolyzed,[2]

$$CaCO_3 + H_2O = Ca'' + OH' + HCO_3'.$$

Letting the chemical symbols represent concentrations, as before,

$$Ca'' \times OH' \times HCO_3' = K_1 \quad (8);$$
$$Ba'' \times OH' \times HCO_3' = K_2 \quad (9);$$

from which it follows that

[1] Ostwald: "Grundriss der allgem. Chem.," p. 427.
[2] Küster: Z. anorg. Chem., **22**, 161.

$$\frac{CaCO_3}{BaCO_3} = \frac{\sqrt[3]{K_1}}{\sqrt[3]{K_2}} \quad (10).$$

That is, in case of complete hydrolysis, the relative solubility of calcium and barium carbonates is equal to the ratio of the cube roots of their solubility products. As will be seen in Table I., the values calculated from expressions (7) and (10) do not differ very greatly in the case of the carbonates.

In our experiments, calcium carbonate was treated with a solution of barium chloride, and barium carbonate with a solution of calcium chloride :

$$CaCO_3 + BaCl_2 \rightleftharpoons BaCO_3 + CaCl_2.$$

When equilibrium has taken place, the solution must be saturated in regard to both calcium and barium carbonates, but the amount of calcium and barium ions is vastly in excess of carbonate ions.

In this solution, disregarding hydrolysis,

$$Ca \times CO_3 = K_1 \quad (11),$$
$$Ba \times CO_3 = K_2 \quad (12),$$

in which K_1 and K_2 represent the same solubility products as in (1) and (2).

The carbonate ions, in their effect on mass action, are common to both the carbonates, so dividing (11) by (12),

$$\frac{Ca}{Ba} = \frac{K_1}{K_2} \quad (13).$$

The same expression is obtained when hydrolysis is assumed to take place.

Since calcium and barium salts have about the same tendency to dissociate, in a solution of the two chlorides the ratio of the calcium ions to the total calcium chloride would be nearly the same as the ratio of the barium ions to the total barium chloride and (13) may, therefore, be written

$$\frac{CaCl_2}{BaCl_2} = \frac{K_1}{K_2} \quad (14).$$

Combining (7) and (14),

$$\frac{CaCO_3}{BaCO_3} = \frac{\sqrt{K_1}}{\sqrt{K_2}} = \sqrt{\frac{CaCl_2}{BaCl_2}} \quad (15).$$

That is, the relative solubility of the carbonates is expressed by the square root of the ratio of the calcium and barium chlorides, in case the pure carbonates did not hydrolyze in water.

Combining (10) and (14),

$$\frac{CaCO_3}{BaCO_3} = \frac{\sqrt[3]{K_1}}{\sqrt[3]{K_2}} = \sqrt[3]{\frac{CaCl_2}{BaCl_2}} \quad (16),$$

or, the relative solubility of the carbonates is expressed by the cube root of the ratio of calcium and barium chlorides, in case the pure carbonates hydrolyzed completely in water.

The latter assumption of complete hydrolysis is probably more nearly correct, as the carbonates are so insoluble. Kohlrausch and Rose[1] found by determining the electrical conductivity, that a liter of water dissolved about 0.25 mg. equivalents of the carbonates at 18°, so that the saturated solutions would be about 0.00025 N. This value is probably not very exact, as the hydrolysis of the salts appears not to have been taken into account and the results given above are omitted from a table of corrected solubilities given later by Kohlrausch.[2] The results indicate, however, that the carbonates are very insoluble. The hydrolysis of solutions containing sodium carbonate has been measured by Shields[3] at 25°. He obtained the following results:

Na_2CO_3 (gram-mols. per liter).	Per cent of hydrolysis.
0.19	2.12
0.094	3.17
0.0477	4.87
0.0238	7.10

While accurate extrapolation for very dilute solutions is impossible from these results, they serve to show that a solution of sodium carbonate as dilute as a saturated solution of calcium carbonate, would be largely hydrolyzed. Calcium car-

[1] Z. physik. Chem., **12**, 234.
[2] *Ibid.*, **50**, 355.
[3] *Ibid.*, **12**, 167.

bonate should hydrolyze to about the extent that sodium carbonate does, as the acid radical is the same and the hydroxides of calcium and sodium are both strong bases. The relative solubility of calcium and barium carbonates would, therefore, be represented more accurately by expression (16) $\sqrt[3]{\frac{CaCl_2}{BaCl_2}}$ than by (15) $\sqrt{\frac{CaCl_2}{BaCl_2}}$.

For the experiments pure calcium and barium carbonates were prepared by precipitating solutions of the chlorides with ammonium carbonate, in excess. Barium carbonate was precipitated from a hot solution. Calcium carbonate was precipitated cold and the precipitate and solution heated to boiling. In this way the salt was obtained in minute calcite crystals, which are more stable than the aragonite obtained by precipitating from a hot solution.[1] The carbonates were thoroughly washed and dried.

Solutions of calcium and barium chlorides, 0.1 N, were prepared and accurately standardized, and from these 0.05 N solutions were made by diluting.

In analyzing solutions containing both calcium and barium chlorides in contact with the carbonates, 25 cc. of solution were drawn off with a pipette through a plug of glass wool. The solution was diluted, acidified with a very few cc. of acetic acid, heated and about 10 cc. of a 10 per cent solution of ammonium chromate added. The latter was prepared from ammonium bichromate, by adding a calculated amount of ammonium hydroxide, not quite sufficient to form the normal salt. The barium chromate formed was allowed to stand, then filtered on a Gooch crucible, ignited and weighed. Calcium could be determined in the filtrate as oxalate, but this was not necessary with the carbonates, as the amount present in a given volume could be calculated when the barium was known. It was necessary to determine both calcium and barium when working with the oxalates and fluorides, on account of their greater solubility.

[1] Z. physik. Chem., 33, 740.

Test analyses on known amounts of barium in the presence of calcium gave excellent results by the method described above.

A preliminary experiment was tried by treating a large excess of calcium carbonate, in a bottle, with a solution of barium chloride, approximately 0.1 N, and in another bottle an excess of barium carbonate with a similar solution of calcium chloride. A small amount of the other carbonate was added in each case. The bottles were shaken for several weeks on a revolving shaft, at room temperature. The following results were obtained:

	Carbonates used.		Initial solution, milligram equivalents per liter.		Final solutions, milligram equivalents per liter.	
	$CaCO_3$. Gram.	$BaCO_3$. Gram.	Ca.	Ba.	Ca.	Ba.
I.	45	0.2±	0.00	100	52	48
II.	0.2±	45	100	0.00	72	28

The final solutions obtained, which should have been alike if equilibrium had been reached, were still very far removed from each other and showed that equilibrium could be reached in this way only very slowly. The experiment showed, however, that for equilibrium the ratio $\frac{Ca}{Ba}$ would lie between $\frac{52}{48}$ and $\frac{72}{28}$. As this experiment had proceeded so slowly, it was evident that very thorough shaking was necessary to make the carbonates react with the chlorides.

We, therefore, did not carry on the experiment in a thermostat, but the bottles containing the mixtures were placed, as before, on a revolving shaft which was running throughout the day, the temperature varying between 15° and 21°. Glass beads or garnets were put in the bottles to keep the precipitate suspended. Without the beads the precipitate tended to harden on the sides of the bottle, due to centrifugal action.

From 200 to 300 cc. of liquid were placed in the bottles with an excess of the carbonates. Instead of starting with pure calcium chloride or barium chloride solutions, the equivalent solutions of these two salts were mixed together in known pro-

portions, so that the ratio $\frac{Ca}{Ba}$ at the beginning was between $\frac{58}{42}$ and $\frac{72}{28}$, the preliminary experiment having shown that final equilibrium would lie between these extremes. In this way much time could be saved in shaking. An excess of each carbonate was used, so that the reaction could proceed in either direction. The mixtures were shaken several weeks. Samples were drawn off at intervals and barium determined till there was no further action apparent. In this manner the results given in Table I. were obtained.

In the last two columns the ratios $\sqrt{\frac{Ca}{Ba}}$ and $\sqrt[3]{\frac{Ca}{Ba}}$ have been calculated from the final solutions obtained and these results are nearly constant. The values do not differ much from each other, but the second expression is probably more nearly correct, so that

$$\text{Relative solubility, } \frac{CaCO_3}{BaCO_3} = 1.20.$$

In the preceding work we have assumed that the carbonates of barium and calcium do not form mixed crystals. In that case only would the solubility relations derived above hold strictly. That each carbonate cannot form an unlimited series of mixed crystals with the other is shown by the fact that the stable crystal form of each is different, calcium carbonate is rhombohedral and barium carbonate orthorhombic. It was probable, however, that the two carbonates could form a limited series of mixed crystals in which each would dissolve a limited amount of the other carbonate. Such mixed carbonates of calcium and barium occur in nature. Should such mixed crystals be produced, the carbonates present in the experiments of Table I. would not be a mechanical mixture of the two pure carbonates, but a mixture of the two carbonates, each saturated with the other, and the relative solubility previously determined would be the relative solubility of these two kinds of mixed crystals. In general, the solubility of a

Table I.

0.1 N $CaCl_2$ and $BaCl_2$.

No.	$CaCO_3$. Grams.	$BaCO_3$. Grams.	Initial solutions, milligram equivalents per liter. Ca.	Ba.	Final solutions, milligram equivalents per liter. Ca.	Ba.	$\sqrt{\frac{Ca}{Ba}}$.	$\sqrt[3]{\frac{Ca}{Ba}}$.
1	40	40	56.83	43.17	63.30	36.70	1.31	1.20
2	40	40	62.01	37.99	63.30	36.70	1.31	1.20
3	40	40	67.15	32.85	62.37	37.27	1.30	1.19
			0.05 N $CaCl_2$ and $BaCl_2$.					
4	20	20	31.16	18.84	31.42	18.58	1.30	1.19
5	20	20	33.50	16.50	32.08	17.92	1.34	1.21

Table II.

0.05 N $CaCl_2$ and $BaCl_2$.

No.	$CaCO_3$. (Grams.)	$BaCO_3$. (Grams.)	Initial solution, milligram equivalents per liter. Ca.	Ba.	Final solution, milligram equivalents per liter. Ca.	Ba.	$\sqrt[3]{\frac{Ca}{Ba}}$.
1	50	0.1±	31.75	18.25	31.89	18.11	1.21
2	0.1±	43.0	31.75	18.25	28.02	21.98	1.08

salt diminishes as the amount of salt with which it forms a mixed crystal increases.[1]

To determine whether or not mixed crystals were formed in the preceding experiments we proceeded in the following manner: A 0.05 N solution of the two chlorides was prepared, in which the salts were present in the proportion required for equilibrium as shown in Table I., Nos. 4 and 5. Part of this solution was treated with barium carbonate, containing a minute amount of calcium carbonate to induce crystallization, and the other part was treated with calcium carbonate containing a very small amount of barium carbonate. In each experiment, then, one carbonate or the other was present in practically pure condition. These mixtures were shaken as before for 2 weeks and the solutions analyzed. In case mixed crystals of the two carbonates had not formed in the previous work, there would be the same solid phases here as before, in Table I., and we should expect no change in the solution. If mixed crystals had formed before, the pure carbonate in excess, in the present experiments, would tend to have a greater relative solubility than indicated in Table I. and the relation of calcium and barium chlorides in solution would change accordingly. The results recorded in Table II. were obtained.

The solution in the first experiment remained practically constant and the same as the final solutions in Table I., showing that calcium carbonate had not taken up an appreciable amount of barium carbonate in the experiments given in Table I. In the second experiment (Table II.) the barium in solution increased and the calcium decreased. As the barium carbonate in this case was practically pure, this result indicates that the barium carbonate in the experiments of Table I. must have taken up a certain amount of calcium carbonate to form mixed crystals.

Summarizing the results in Table II.,

$$\text{Relative solubility } \frac{\dfrac{CaCO_3}{BaCO_3 \text{ saturated with } CaCO_3}}{\dfrac{CaCO_3 \text{ dissolved in } BaCO_3}{BaCO_3}} = 1.21, \quad = 1.08.$$

[1] Roozeboom: Z. physik. Chem., 10, 145.

The average of these values should represent very nearly the relative solubility of the two pure carbonates, or

$$\text{Relative solubility } \frac{CaCO_3}{BaCO_3} = 1.15.$$

This result, allowing for mixed crystals, differs but little from the one in which no allowance was made.

Calcium and Barium Oxalates.

As oxalic acid is a comparatively strong acid, the hydrolysis of the oxalates with water can be neglected, and an expression similar to that for the carbonates, when hydrolysis is assumed to be absent, can be used to represent the relative solubility of barium and calcium oxalates:

$$\frac{CaC_2O_4}{BaC_2O_4} = \frac{\sqrt{K_1}}{\sqrt{K_2}} = \sqrt{\frac{CaCl_2}{BaCl_2}}.$$

K_1 and K_2 represent the solubility products of the respective oxalates.

It was found that barium oxalate is much more readily soluble than calcium oxalate so that the reaction

$$BaC_2O_4 + CaCl_2 = CaC_2O_4 + BaCl_2$$

is very nearly complete. In fact, barium oxalate has an appreciable absolute solubility, and it was necessary to determine the amount of both calcium and barium in solution, although solutions of known concentration of the chlorides were used as before.

The oxalates were prepared by precipitating the chlorides from a hot solution with ammonium oxalate, in excess. They were thoroughly washed and dried. Solutions of barium and calcium chlorides, 0.1 N and 0.05 N, were used, as before.

The results obtained are given in Table III. The first two experiments were preliminary and only barium was determined directly. In the others, both barium and calcium were determined. Experiments 3 to 6 were shaken about 3 weeks.

Table III.

No.	CaC_2O_4. (Grams.)	BaC_2O_4. (Grams.)	Initial solution, milligram equivalents per liter. Ca.	Ba.	Final solution, milligram equivalents per liter. Ca.	Ba.	$\sqrt{\frac{Ca}{Ba}}$.
			0.1 N $CaCl_2$ and $BaCl_2$.				
1	15.00 g.	0.2± g.	00.00	100	. .	97.35	
2	0.2±	20.00	100.0	00.00	. .	95.84	
3	15.0	0.2	3.41	96.59	3.43	100.8	0.18
4	0.2	15.0	3.41	96.59	2.48	98.87	0.16
			0.05 N $CaCl_2$ and $BaCl_2$.				
5	15.0	0.2±	00.0	50.0	4.00	47.83	0.29
6	0.2±	20.0	50.0	00.0	2.86	50.35	0.23

The agreement between the 0.1 N and 0.05 N solutions is not very satisfactory, but is largely due to the fact that the amounts of calcium in solution were small, and small errors in determination would give relatively large errors in the ratio. It will be observed that, in the last 4 experiments, the final equilibrium appears not to be independent of the quantities of barium and calcium oxalates. With an excess of calcium oxalate the ratio $\frac{Ca}{Ba}$ is greater than with an excess of barium oxalate. Apparently mixed crystals form to a certain extent, which would account for this, but the error from this cause is not greater than the other errors of the experiment.

Taking the average of the 4 results,

$$\text{Relative solubility } \frac{CaC_2O_4}{BaC_2O_4} = 0.22.$$

Calcium and Barium Fluorides.

The attempt was made to measure the relative solubility of calcium and barium fluorides, but the results are only of qualitative interest.

Barium fluoride was made by nearly neutralizing pure hydrofluoric acid with potassium carbonate and treating this solution with a dilute solution of barium chloride, which was not quite sufficient to precipitate all the fluoride. Care was taken that the barium chloride was not added in excess, as a double barium chloride and fluoride apparently precipitated under these conditions. The precipitated barium fluoride was thoroughly washed and dried.

The calcium fluoride used was pure fluor spar, very finely ground.

As these fluorides form three ions in dilute solution, the relative solubility would be represented by an expression similar to that for the hydrolyzed carbonates.

$$\frac{CaF_2}{BaF_2} = \frac{\sqrt[3]{K_1}}{\sqrt[3]{K_2}} = \sqrt[3]{\frac{CaCl_2}{BaCl_2}}.$$

On treating barium fluoride with calcium chloride it was found that the reaction

$$BaF_2 + CaCl_2 = CaF_2 + BaCl_2$$

was nearly complete, and the amount of calcium left in solution was too small to determine accurately. Barium fluoride is, therefore, very much more soluble than calcium fluoride, but the relation $\sqrt[3]{\frac{CaCl_2}{BaCl_2}}$ is so much affected by slight errors in determining calcium, that reliable quantitative results on the relative solubility of the two fluorides cannot be obtained.

Only 0.05 N solutions of calcium and barium chlorides could be used. A 0.1 N solution reacted with barium fluoride and formed a double fluoride and chloride, removing barium chloride from solution. The results obtained were as follows:

Table IV.

0.05 N $CaCl_2$ and $BaCl_2$.

No.	CaF_2. (Grams.)	BaF_2. (Grams.)	Initial solution, milligram equivalents per liter. Ca.	Ba.	Final solution, milligram equivalents per liter. Ca.	Ba.
1	15.0	0.5±	0.0	50.0	1.36	61.72
2	0.5±	15.0	50.0	0.0	2.00	61.60

The absolute solubility of the carbonates and oxalates of calcium and barium has been determined by Kohlrausch and Rose and by Kohlrausch,[1] by means of the electrical conductivity of the saturated solutions, and the relative solubilities can be calculated from their results and compared with ours. They worked at 18°.

	Solubility, milligram equivalent per liter.	$\frac{Ca}{Ba}$ (Kohlrausch.)	$\frac{Ca}{Ba}$ (Foote and Menge.)
$CaCO_3$	0.26	1.08	1.15
$BaCO_3$	0.24		
CaC_2O_4	0.087	0.11	0.22
BaC_2O_4	0.76		

Considering that the results are obtained by two totally different methods, the agreement is as close as could be expected. The method which we have used we believe gives closer results than the conductivity method for the carbonates where

[1] Z. physik. Chem., 12, 234; 50, 355.

the ratio is not far from 1, for slight errors in determining the amounts of calcium and barium in solution would not materially affect the ratio. On the other hand, in the case of the oxalates, the Kohlrausch method should give fully as good results, for by our method a slight error in determining the quantity of calcium, which is present in solution in small amounts, affects the ratio considerably.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.,
February, 1906.

THE BEARING OF HYDRATES ON THE TEMPERATURE COEFFICIENTS OF CONDUCTIVITY OF AQUEOUS SOLUTIONS.

[SIXTEENTH COMMUNICATION.]

BY HARRY C. JONES.

That the electrical conductivity of aqueous solutions of electrolytes, in general, increases greatly with rise in temperature is a well known fact. This might be due either to an increase in the dissociation of the electrolyte with rise in temperature, or to an increase in the velocity with which the ions move, or to both. It is not a difficult matter to test the effect of change in temperature on the dissociation of electrolytes. It is only necessary to measure the dissociation directly, at different temperatures, by the conductivity method. This has been done recently by Jones and West,[1] for temperatures ranging from 0° to 35°. The result is that electrolytes, in general, are *slightly less* dissociated at the higher than at the lower temperatures.

As has been pointed out, this is in accord with the theory of Dutoit and Aston, which makes the dissociating power of a solvent a function of its own association—the more associated a solvent the greater its dissociating power. Take a solvent like water, the higher the temperature the less it is associated and, consequently, the smaller its power to break molecules of electrolytes down into ions.

Having eliminated the factor of dissociation as increasing the conductivity of electrolytes at the higher temperature, we are

[1] THIS JOURNAL, 34, 357 (1905).

forced to conclude that the increase in conductivity with rise in temperature, shown by solutions of electrolytes in general, is due to an increase in the velocities with which the ions move.

There are a number of factors which determine the velocity with which an ion moves through a solution of an electrolyte. Assuming that the force which drives the ions is constant, *the velocity would be conditioned chiefly by the viscosity of the medium through which the ion passed, and by the size of the ion.* At the more elevated temperature the force which drives the ion would be greater, and the viscosity of the medium through which the ion moves would be less. Both of these factors would increase the velocity with which the ions move and, consequently, increase the conductivity as the temperature was raised.

The object of this paper is to call attention to another factor which causes the ions to move faster at the more elevated temperature. *The mass of the ion decreases with rise in temperature.* This does not refer to the charged atom or group of atoms which we usually term the ion, but to this charged nucleus plus a larger or smaller number of molecules of water, which are attached to it, and which it must drag along with it in its motion through the remainder of the solvent.

That ions are hydrated has been shown beyond question by Jones and his co-workers. That these hydrates are relatively unstable compounds has also been demonstrated; the higher the temperature the less complex the hydrates existing in the solution. This can be seen from one example. In a solution of a certain definite concentration, every molecule of calcium chloride, or the ions resulting from it, holds about 30 molecules of water. From such a solution practically all of the water can be removed by simply boiling it, except 6 molecules of water to 1 of calcium chloride—this number being brought out of the solution by the salt as water of crystallization. The higher the temperature, then, the less complex the hydrate formed by the ion. The less the number of molecules of water combined with the ion the smaller the mass of the ion, and the less its resistance when moving through the solvent.

Consequently, the ion will move faster at the high temperature. This conclusion can be tested by the results of experiment. If this factor of diminishing complexity of the hydrate formed by the ion with rise in temperature, plays any prominent rôle in determining the large temperature coefficient of conductivity, then we should expect to find *those ions with the largest hydrating power, having the largest temperature coefficients of conductivity*. This will readily be seen to be the case. The more complex the hydrate, *i. e.*, the greater the number of molecules of water combined with an ion, the greater the *change* in the complexity of the hydrate with rise in temperature. We can readily test this conclusion by the results of the experimental work of Jones and West.[1] Let us compare the temperature coefficients of conductivity per degree rise in temperature, for some of those substances which have slight hydrating power, with the corresponding coefficients for a few of the substances which have a much greater power to combine with water.

The volumes for which the comparisons are made range from 2 to 1024, and the temperatures from 25° to 35°.

A comparison of Table I. and Table II. will show that the above conclusion is confirmed by the experimental results. The substances included in Table I. have very slight hydrating power. Those in Table II. have very much greater hydrating power. It will be remembered that hydrating power is a function of water of crystallization—the larger the number of molecules of water of crystallization the greater, in general, is the hydrating power of the substance. It will be seen that the substances in Table I. have little or no water of crystallization, while those in Table II. crystallize with large amounts of water. The water of crystallization may be taken as roughly proportional to the hydrating power of the substance.

The substances in Table I. have much smaller coefficients of conductivity than those in Table II., even taking into account the fact that those in Table II. are ternary electrolytes, while those in Table I. are binary electrolytes.

[1] THIS JOURNAL, 34, 357 (1905).

Table I.—Substances with Slight Hydrating Power.

	Temperature coefficients in conductivity units.	
	$v = 2.$	$v = 1024.$
Ammonium chloride	2.07	2.94
" bromide	2.16	2.86
Potassium chloride	2.13	2.84
" bromide	2.18	2.91
" iodide	2.09	2.91
" nitrate	1.86	2.71

Table II.—Substances with Large Hydrating Power.

	$v = 2.$	$v = 1024.$
Calcium chloride	3.11	5.61
" bromide	3.01	5.20
Strontium "	2.93	5.27
Barium chloride	2.86	5.30
Magnesium chloride	2.55	4.59
Manganese "	2.37	4.86
" nitrate	2.24	4.16
Cobalt chloride	2.54	4.95
" nitrate	2.48	4.67
Nickel chloride	2.63	5.04
" nitrate	2.51	4.58
Copper chloride	2.15	5.04
" nitrate	2.38	4.88

Another fact, of equal importance, is brought out by comparing the results in Table I. with one another, and similarly those in Table II. with one another. If the temperature coefficient of conductivity is a function of the decrease in the complexity of the hydrate formed by the ion, with rise in temperature, then we should expect that *those substances which have equal hydrating power would haxe approximately the same temperature coefficients of conductivity.*

If we examine the above tables we shall see that this is true. The substances in Table I. all have only very slight hydrating power, as would be expected from the fact that they all crystallize without water. Their temperature coefficients of conductivity are all of the same order of magnitude and, indeed, are very nearly equal.

The substances in Table II. all have very great hydrating power, and all have a hydrating power of the same order of

magnitude. This would be expected, since nearly all of these substances crystallize with 6 molecules of water. There are a few compounds in this table calling for special comment. Barium chloride crystallizes with only 2 molecules of water, yet it forms hydrates comparable with those substances with larger amounts of water of crystallization. It is, therefore, perfectly in keeping with the above relation that its temperature coefficients of conductivity should be of the order of magnitude that they are in the above table.

Manganese chloride crystallizes with only 4 molecules of water, but the work of Jones and Bassett[1] shows that it forms hydrates about as complex as the other salts in Table II. Its temperature coefficients of conductivity are of the same order of magnitude as the other substances in this table.

Of the compounds recorded in Table II., the one which, apparently, presents the most pronounced exception to the relation that we are now considering, is copper chloride. This salt crystallizes with only 2 molecules of water, and yet has a temperature coefficient of conductivity that is nearly as large as the salts with 6 molecules of water of crystallization. It might be inferred that this salt has much less hydrating power than the others in Table II. The work of Jones and Bassett[2] shows that this is not the case. Copper chloride has a large hydrating power, indeed much larger than would be expected from the amount of water with which it crystallizes. Its temperature coefficient of conductivity is, therefore, not surprisingly great.

A third point that is brought out by the results in the above tables, is the following: *At the higher dilution the temperature coefficient of conductivity for any given substance is greater than at the lower dilution.* That this is a general relation will be seen by reference to the work of Jones and West.[3] This is explained very satisfactorily on the basis of the suggestion made in this paper. The complexity of the hydrate at the higher dilution is greater than at the lower dilution, as is shown by the experi-

[1] THIS JOURNAL, 33, 562 (1905).
[2] *Ibid.*, 33, 577 (1905).
[3] *Ibid.*, 34, 357 (1905).

ments of Jones and his co-workers[1] on the composition of the hydrates formed by different substances at different dilutions.

The hydrate being more complex at the higher dilution, the change in the composition of the hydrate with change in temperature would be greater at the higher dilution and, consequently, the temperature coefficient of conductivity is greater the more dilute the solution.

The three points that are established in this paper are :

1. The temperature coefficients of conductivity of aqueous solutions of electrolytes are greater, the greater the hydrating power of the electrolyte.

2. The temperature coefficients of conductivity of aqueous solutions of electrolytes are of the same order of magnitude for those substances having, approximately, the same hydrating power.

5. The temperature coefficients of conductivity, for any given substance, increase with the dilution of the solution, and this increase is greatest for those substances with large hydrating power.

All three of these conclusions are necessary consequences of the assumption that the *large change in conductivity with change in temperature is due, in part, to the decreasing complexity of the hydrates formed around the ions*, with rise in temperature. Since these conclusions are all verified by the results of experiment, we must accept the assumption which led to them as containing a large element of truth.

It is more than probable that the decreasing complexity of the hydrates, with rise in temperature, is a very important factor in conditioning the large temperature coefficients of conductivity, especially of those substances which have large hydrating power.

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[1] THIS JOURNAL, 33, 534 (1905) ; 34, 290 (1905).

AN ELECTRICAL METHOD FOR THE SIMULTANEOUS DETERMINATION OF HYDROGEN, CARBON AND SULPHUR IN ORGANIC COMPOUNDS.

By H. N. Morse and C. W. Gray.

In No. 8, Vol. I., 1906, page 699 of the *Chemischer Central-Blatt*, which has just come into our hands, we find an account of a "New Method for the Analysis of Organic Compounds," by Oreste Carrasco. The original description appeared in *Atti R. Accad. dei Lincei Roma* [5], **14**, II., 613, December 3, 1905. It is stated, however, by the one making the abstract for the *Central-Blatt*, that an account of the method was deposited July 30, 1904, in the form of a "sealed communication," which was opened for the first time at the meeting of November 19, 1905.

The method in question is quite similar to one which was described in this Journal, Vol. 33, No. 6, which appeared June 1, 1905, by H. N. Morse and L. S. Taylor, under the title, "An Electrical Method for the Combustion of Organic Compounds." The account of the method of Morse and Taylor was delivered by them in manuscript to the editor of the Journal on March 1, 1905, as appears at the close of the published article, and at that time the method had been fully developed, as is attested by the introductory statements of its authors, as follows: "The process for the Analysis of Organic compounds which is here described has been in general use in this laboratory during the past year and with such satisfactory results that it has almost wholly supplanted the older method of burning organic compounds." In other words, the process in question came into general use in this laboratory early in the year 1904, as early, in fact, as March 1 of that year. Its feasibility must, of course, have been demonstrated at a still earlier date. The idea of the method originated in connection with some work of one of the authors with J. C. Frazer upon "A New Electric Furnace and Various Other Heating Appliances for Laboratory Use," an account of which

was published in this JOURNAL, **32**, 93, and the first experiments with the process were made by him during the year 1903. To sum up the facts having a bearing on the question of priority, it appears :

1. That the method of Morse and Taylor was published on June 1, 1905, and that of Carrasco on December 3, 1905.

2. That the former process had been developed and was in use in this laboratory as early as March 1, 1904, while an account of the latter process—obviously still in an incomplete state—was deposited in the form of a "sealed communication" on July 30, 1904, which was opened for the first time on November 19, 1905.

We now proceed to describe an extension of the method of Morse and Taylor to the simultaneous determination of carbon, hydrogen and sulphur.

The apparatus which is employed is represented in Figs. I. and II. It is identical with that described by Morse and Taylor,[1] except in so far as modifications were made necessary for the purpose of determining sulphur at the same time with carbon and hydrogen. It consists of a thin, hard glass tube open at both ends and having a length of about 600 mm. and an internal diameter of about 20 mm. One end is closed with a rubber stopper through which pass (I.) the small porcelain tube E, having a length of 300 mm. and an external diameter of 6 mm. and (II.) the exit tube L. The T-tube D is slipped over the end of the porcelain tube and is fastened to the latter by means of a short piece of rubber tubing. The horizontal end of D is closed with a stopper through which passes a platinum wire. The wire extends through the whole length of the porcelain tube and returns upon the outside in a series of suspended loops, and then passes out through the rubber stopper, as shown in the figure. The ends of the wire are much thicker than the intermediate portion, in order to avoid the danger of burning the stoppers. To this point the new apparatus is identical with the older one. The first modification which was introduced to adapt the method to the determination of sulphur was to wind the coils in the vicinity of G

[1] THIS JOURNAL, **33**, 591.

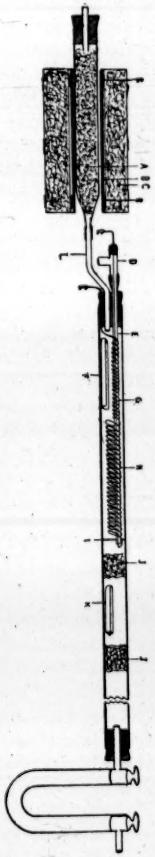


FIG. I.

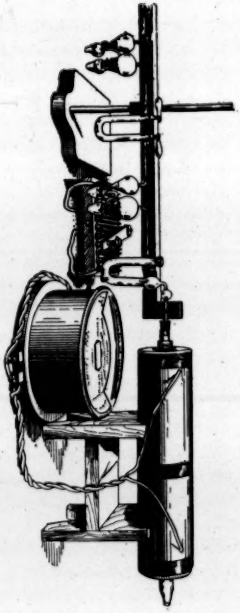


FIG. II.

tightly about the porcelain tube, in order to make room for the long platinum boat F, which, when an analysis is to be made, contains a weighed quantity of pure peroxide of lead. The rear end of the boat is open to facilitate contact between the products of combustion and the oxide. The second change was to remove the rolls of oxidized copper wire gauze which formerly preceded and followed the boat K, and to substitute in their places the asbestos plugs J and J. The rear end of the porcelain tube passes through the eccentrically perforated platinum disk I, and is thereby maintained in its proper position in the glass tube.

The apparatus A B C, in front of the combustion tube, is one designed to complete the absorption of oxides of nitrogen, a portion of which is also retained by the peroxide in F. It consists of the graphited porcelain tube B, which has a length of about 300 mm. and is electrically heated, the asbestos covering C and the glass tube A, which is filled with asbestos covered with peroxide of lead. The tube A is connected on the one side with the combustion tube and on the other with the usual absorption apparatus for water and carbon dioxide.

The method of graphiting porcelain tubes, like B, and other objects for the purpose of electrical heating, has been described by Morse and Frazer,[1] and the procedure need not, therefore, be explained in this connection. To prepare the tube A, asbestos is covered, by sprinkling and mixing, with as much peroxide of lead (which has previously been heated to nearly 300°, *i. e.*, to the temperature necessary for complete dehydration) as can be made to adhere to it; and, after filling the tube, an additional quantity of the peroxide is sifted in among the asbestos fibers. A single filling suffices for a very large number of analyses. During a combustion it is necessary to maintain in the tube A a temperature of about 175°, in order to insure the complete absorption of nitric oxide. The apparatus must, therefore, be subjected to a species of calibration before it is used. To this end a current of dried air, approximately equal to that of the gas which normally flows through an apparatus during a combustion, is passed through

[1] This Journal, 32, 93.

A. A thermometer is inserted and the amount of current necessary to maintain a series of temperatures in the tube, *e. g.*, 100°, 125°, 150°, 175° and 200°, is ascertained. Furthermore, the length of time required by a given current to bring the contents of the tube to a constant temperature is determined. A calibration of this kind is not precise, since the rate of flow of gas during a combustion is irregular and at all times of somewhat uncertain magnitude, but it is sufficiently accurate for all practical purposes.

The peroxide of lead which is employed in F for the absorption of the oxides of sulphur is prepared by the method of Dennstedt in the highest practicable state of purity, and is subsequently heated to 300° to insure complete dehydration. The quantity of PbO which a unit weight of it will yield is determined with care, once for all, by heating weighed quantities of the peroxide to constant weight in a current of nitrogen, and the result is employed in finding the amount of sulphur trioxide produced in the combustion. It is necessary, of course, that the peroxide, when weighed, shall be entirely free from moisture; we therefore proceed in the following manner: The boat F, after introducing the requisite amount of the peroxide—about 5 grams—is placed in a horizontal position in a glass weighing tube having a ground glass stopper, the material, boat and tube are then heated for half an hour at a temperature of 120°, and afterwards cooled in a desiccator. When the desiccator is opened for the purpose of weighing, the tube is immediately closed with the stopper.

The procedure, when an analysis is to be made, is as follows: The boat containing the weighed quantity of peroxide is inserted at F, and that containing the substance to be burned at K. The two circuits—that through the combustion apparatus and also that through A B C—are closed through regulating rheostats, and dry air is passed through the whole apparatus—except, of course, the absorption train. The current through A B C is allowed to rise quickly to the quantity which is known to produce in A the most effective temperature for the absorption of nitric oxide—about 175°—while the current through the combustion apparatus is regulated more cautiously,

especially if there is danger of indirectly heating the substance in K to a temperature at which it becomes volatile. Having dried out the whole apparatus, the absorption train is joined to A, the current of dried and purified air entering at the rear is continued, oxygen is admitted at D, and the substance in K—also the plug of asbestos J in front of the boat—is heated by a lamp held in the hand. The flow of oxygen and of air, and the heating of the substance with the lamp, likewise the temperature of the platinum coils, are, thereafter regulated according to the best judgment of the operator. If the substance is so volatile that an explosion is likely to occur between the asbestos plugs, the air admitted at the rear is deprived of its oxygen by inserting a roll of copper wire gauze behind the last asbestos plug and heating it with a lamp appropriately placed under the tube, or nitrogen, instead of air, is passed in from a gasometer.

The platinum coils are maintained at a moderately bright red heat during a combustion. This insures a sufficiently high temperature of the peroxide under the small coils at G, and is ample for the combustion of the vapors of the substance.

The precautions which are taken to prevent the cracking of the glass combustion tube, especially during the cooling-down period, have been sufficiently described in a previous paper,[1] and only one of these will be recalled here—that of blackening the whole of the exposed portion of the tube with a smoky flame as soon as the combustion is finished, and before reducing the current flowing through the platinum wire.

The material in the boat consists, after a combustion, of a mixture of lead peroxide, lead sulphate, and—if the substance contained nitrogen—a small quantity of lead nitrate; and the amount of PbO—supposing all of the lead to be in that state—is known. To find the amount of sulphur, reckoned as SO_3, it is, therefore, only necessary to reduce the peroxide and nitrate in the mixture to oxide and weigh the residue. This reduction is effected in the following manner: The boat, with its contents, is placed in a hard glass tube, and behind it is inserted a roll of copper wire gauze. Both the boat and the roll

[1] THIS JOURNAL, 33, 591.

are heated by lamps and air is passed through the tube; or the reduction is effected in a current of nitrogen flowing from a gasometer. The decomposition of the nitrate is made manifest by the appearance and subsequent disappearance of reddish vapors, and the reduction of the peroxide by the disappearance of brown and red colors in the material; nevertheless, the residue is reheated, after weighing, in an atmosphere of nitrogen to ascertain if the weight remains constant.

We give below the results obtained by the analysis of a few substances:

"Sulphonal," $(CH_3)_2C(SO_2C_2H_5)_2$.

	C.	H.	S.
Theoretical	36.80	7.06	28.09
Found	36.69	7.26	28.16
"	36.47	7.12	27.90
"	36.73	7.19	28.03

Phenylthiourea, $NH_2CSNHC_6H_5$.

	C.	H.	S.
Theoretical	55.19	5.29	18.44
Found	55.40	5.24	18.30
"	55.24	5.50	18.53

Phenylthiosemicarbazide, $C_6H_5NHNHCSNH_2$.

	C.	H.	S.
Theoretical	50.22	5.12	19.17
Found	50.38	5.40	18.91
"	50.39	5.50	19.31

Parasulphaminebenzoic Acid, $C_6H_4(SO_2NH_2)COOH$.

	C.	H.	S.
Theoretical	41.76	3.50	15.93
Found	41.84	3.70	16.05
"	41.79	3.57	16.10

In the original form of the method as described by Morse and Taylor[1] for the determination of carbon and hydrogen only, the oxides of nitrogen were reduced by means of metallic copper, and such a reduction, in skilled hands, is practicable and gives satisfactory results, but further experience has shown that this procedure is apt to fail in the hands of be-

[1] THIS JOURNAL, 33, 591.

ginners. In the later practice, therefore, the use of copper has been abandoned, and the oxides of nitrogen are now absorbed by the peroxide of lead in exactly the manner described above. If carbon and hydrogen are to be determined in a compound containing nitrogen but no sulphur, the boat of peroxide at F may be dispensed with and the contents of A relied upon to absorb all the oxides of nitrogen. It is well, however, in burning substances which do not contain sulphur, to replace the plugs of asbestos J J by oxidized rolls of copper wire gauze.

It is stated by Carrasco that his method, in the form described in the "sealed communication"—that is, without any provision for the removal of oxides of nitrogen, "is adapted to substances containing ammoniacal nitrogen, while in the presence of NO_3 groups too high values for carbon are obtained," etc. The first part of the above statement, which is quoted from the abstract in the *Central-Blatt*, is surprising in view of the fact that probably all organic substances containing "ammoniacal" nitrogen yield nitric oxide when burned in oxygen, and many of them notable quantities of it. It would seem that even a little actual experience with his proposed method, as applied to nitrogenous substances, should have convinced its author that, when any compound containing nitrogen, whatever its class, is burned for the purpose of determining carbon and hydrogen, it is wise to make ample provision for the reduction or absorption of oxides of nitrogen.

JOHNS HOPKINS UNIVERSITY,
March 14, 1906.

REPORTS.

The Atomic Weight of Nitrogen.

In the last report, for 1906, of the International Committee on Atomic Weights, attention is called to recent work on chlorine and nitrogen which indicates that an entire revision of the atomic weights may soon be necessary, because nearly all of them are based on the assumed accuracy of a few, such as those of silver, chlorine, bromine, sodium, etc., some of which have been changed as a result of the use of improved and more accurate methods. In the report refer-

ence also is made to the fact that nearly all the weights are based on the analyses of several oxyhalogen salts. "Their accuracy is assumed and all the anomalies, which appear in determinations based upon other lines of research, are commonly ascribed to undiscovered errors. The assumption may be sustained, but it is not yet beyond the reach of criticism." Among the atomic weights which have been redetermined by the more accurate and logical methods is that of nitrogen. The results obtained by independent workers, using different substances and both gravimetric and volumetric methods, necessitate the acceptance of the value 14.01 instead of the value 14.04, as found by the indirect gravimetric methods, and as adopted by the International Committee on Atomic Weights. This work upon the atomic weight of nitrogen has been carried out by Guye[1] and his colleagues at Geneva, and by Gray,[2] in Sir Wm. Ramsay's laboratory and in the Chemical Institute in Bonn. The basis of the present report is a lecture on the subject delivered by Guye, last year, before the chemical society of Paris. The fact is pointed out that, in the methods used by Stas and his predecessors and followers, as shown in Table I., the values are not very concordant and are generally higher than the values in Table II., which are based upon determinations of the densities of the gases, corrected by physical-chemical methods.

Table I.—From Chemical Data.

				Atomic weight.
Marignac	(1843)			14.043
Stas	(1865)			14.055
Dean	(1900)	ratio	$AgCN : Ag$	14.031
Scott	(1901)			14.010
Thomsen	(1894)	"	$HCl : NH_3$	14.021
Hardin	(1896)	"	$Ag : AgNO_3$	14.01
Richards and Archibald	(1904)	"	$CsNO_3 : CsO_{\frac{1}{2}}$	14.037
		"	$KNO_3 : K_2O_{\frac{1}{2}}$	14.040

Table II.—From Physical Data.

		Gases compared.	Method of correction.	Atomic weight.
Rayleigh	(1905)	N_2 and O_2	Limiting densities	14.009
		N_2O " O_2	" "	13.996
Berthelot	(1898)	N_2 " O_2	" "	14.007
Leduc	(1897)	N_2 " O_2	Molecular volumes	14.005
Jaquerod and Perrot	(1905)	N_2 " O_2	Comparison at high temperatures	14.008

[1] Bull. Soc. Chim., [3], **33**, 44 (1905).
[2] J. Chem. Soc., **87**, 1601 (1905).

Guye points out that the methods which have been used in determining the atomic weight of nitrogen gravimetrically introduce a number of uncertain factors, and increase the probable error of the result. Thus, in the case when the value is determined from a study of the ratio $Ag : NH_4Cl$, he shows that the atomic weight determined can be expressed by the following equation:

$$X = Ar - B.$$

When r is the ratio of the silver and ammonium chloride, A the assumed known atomic weight of silver, and B the sum of the atomic weights of $4H + Cl$. While the value for r can be determined with considerable accuracy, those for A and B involve greater errors, especially as nearly all of the atomic weights are based on that of silver, and an error here would produce a greater error in the atomic weights of the other substances whose weights have been determined by reference to it. Guye concludes that the errors in the atomic weight of nitrogen, as determined by the classical methods of Stas and his predecessors and followers, vary from ± 0.013 to ± 0.039, and that these methods cannot be used to determine the atomic weight of nitrogen with accuracy in the second decimal place.

On the other hand, by the use of modern physical-chemical methods, very concordant and accurate determinations can be made. These values are obtained by determining the ratio of the density of nitrogen to that of other gases, the results being then corrected with due regard to the laws of Boyle, Avogadro, etc. The methods used to correct the densities found are:

(*a*) The reduction of the critical constants;
(*b*) The method of limiting densities;
(*c*) The method of corresponding densities;
(*d*) The method of the molecular volumes.

In this manner results are obtained in which the error is only ± 0.003.

The atomic weight of nitrogen as determined by these methods is 14.008, as shown by the following summary of the results:

Ratio of	N_2 and O_2	(6 determinations)		14.009
" "	N_2 " CO	(6 ")		14.006
" "	N_2O " CO_2	(2 ")		14.007
" "	NO " O_2	(2 ")		14.008
		General average,		14.008

While the older gravimetric methods used to determine the atomic weight of nitrogen are not accurate, owing largely to their unfortunate selection, it is possible to choose substances where both the direct weights and volume relations can be determined in the same substance.

Guye has thus been able, using nitrous oxide, to determine the atomic weight of nitrogen by the two methods. A glass tube, containing a spiral of iron wire, connected by platinum loops fused in the ends of the tube, is first exhausted and weighed, then filled with pure dry nitrous oxide and weighed. If a current is then passed through the spiral the gas is decomposed and the nitrogen formed is absorbed in a tube of cocoanut charcoal, which has been carefully exhausted. The weight of the nitrogen can thus be determined, as can that of the oxygen, by the increase of weight of the tube containing the spiral. This, of course, is a very brief outline of the method and gives no idea of the immense difficulties which had to be overcome before it could be used. The average of one series of 5 determinations was 14.007, while another, of 3 determinations, gave 14.004.

In the analysis by volume the same apparatus was used to decompose the gas. The vessel, to which a manometer was attached, was filled with nitrous oxide, which, after its pressure had been determined, was decomposed. By observing the change in pressure, keeping the volume constant, the necessary data could be obtained from which to calculate the atomic weight. The mean of 4 determinations by this method gave 14.015, which, averaged with the analyses by weight, gives a mean of 14.009, as compared with the atomic weight 14.008 by the physical-chemical method.

Analysis by weight of N_2O	(5 determinations)	14.007
" " " "	(3 ")	14.003
" " volume " "	(6 ")	14.015
		14.009

That this figure or, in round numbers, 14.01, is more correct than 14.04 is confirmed by the work of Gray, who used nitric oxide, which was obtained free from nitrous oxide ane nitrogen. Tne nitrous oxide was removed by allowing the impure nitric oxide gas to bubble through several vessels containing liquid nitric oxide in which the nitrous oxide was absorbed. The nitrogen was separated by subliming the nitric oxide containing nitrogen at a low pressure and removing the nitrogen, which was not absorbed under these conditions, by the pump.

The gas thus obtained was carefully tested for impurities, its density was determined and the value corrected to reduce it to that which it would have as a perfect gas, and also to obtain the atomic weight of nitrogen by the gravimetric method. The apparatus used by Gray consisted of a vessel which could be exhausted, it contained a porcelain boat resting upon nickel supports; these served as the two poles of a source of electricity which was used to heat the contents of the boat by means of a platinum wire wound around the boat and connected with the nickel wires. Carefully purified nickel, in a finely divided condition, was placed in the boat. The known weight of nitric oxide could be decomposed by contact with the heated nickel, the free nitrogen absorbed in charcoal and weighed, and the oxygen determined by the increase in weight of the bulb and boat.

The results obtained by this method may be summarized in the following table:

I. From the density of nitric oxide corrected by two different methods, 12 results	14.006
II. From the density of nitrogen gas obtained in the gravimetric analysis, 2 results	14.008
III. From the gravimetric analysis of nitric oxide, 22 results	14.010
General average, giving each result an equal value	14.0085

From an examination of Tables I. and II. it will be seen that the physical-chemical methods give, in general, more concordant and lower results than the chemical methods. Guye suggests that possibly this may be due to an error in the atomic weight of silver and presents the following arguments in favor of a lower value:

Recalculating 60 determinations of the ratio of silver to silver salts, using the figure 14.01 for nitrogen, the average result for silver is 107.885.

While the atomic weights of carbon, nitrogen and hydrogen have been accurately determined by the physical-chemical methods, those of chlorine, sulphur and phosphorus have been obtained by the use of only one gas in each case, and the results have not yet been verified. If these weights are used to recalculate a number of determinations, an average of 107.905 is obtained for silver.

Dixon and Edgar have determined the atomic weight of chlorine by a direct synthesis of hydrochloric acid, from hydro-

gen and chlorine; they obtain the value 35.463. The use of this weight in the recalculation of the atomic weight of silver gives the figure 107.88.

From a consideration of all these facts Guye suggests that the difference in the atomic weight of nitrogen, as obtained by the older gravimetric methods and by the physical-chemical methods, may be due to the use of too high an atomic weight for silver, which probably lies between 107.871 and 107.895, and cannot be as high as 107.93, the value adopted by the Committee on Atomic Weights. J. E. G.

The Action of Ozone on Organic Compounds.

Since the discovery of ozone by Schoenbein, in 1840, its action on various organic substances has been investigated by a considerable number of chemists. The results, hitherto, have not been very satisfactory, nor have they led to conclusions of general interest. This has arisen, in part, from the difficulty of obtaining ozonized oxygen of sufficiently constant composition and with the necessary concentration of ozone, in part, however, from the explosive nature of the products of the reaction. The results may be summarized by saying that ozone was known to act on various hydrocarbons such as methane and ethylene, and on alcohol, forming aldehydes, acids and hydrogen peroxide, while, under certain conditions, explosive products of the nature of peroxides were formed, which were decomposed by water in a highly complicated fashion.

Some time ago C. Harries, professor at the University of Kiel, noticed how readily ozone attacks rubber, a fact which is well known to all who have worked with ozone, but on treating pure caoutchouc with it he obtained no reaction. By means of an alternating current of high voltage, the ozone content of the gas was raised to about 5 per cent; this gaseous mixture readily acted on caoutchouc, but the product is too complicated to be of service, at present, in the elucidation of the constitution of the parent substance.

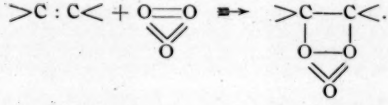
Harries, in conjunction with a number of co-workers, then investigated, in a systematic manner, the action of ozone on various classes of organic compounds; most of the results have been published, at intervals, in brief papers, but recently they have been embodied in a single article[1] of considerable interest.

The experiments were carried out by dissolving the substance under examination in most carefully dried chloroform, cooling the solution in a freezing mixture and passing through it a stream of ozonized oxygen and carbon dioxide. The lat-

[1] Ann. Chem. (Liebig), **343**, 311.

ter serves to remove volatile products and to diminish the danger of explosion. The chloroform appears to have a similar influence.

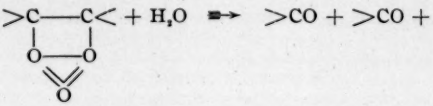
In these circumstances ozone is found to combine with compounds containing an ethylene linkage, forming "ozonides," a term which has been applied previously by Schoenbein to silver peroxide :



It will be noticed that Harries formulates the oxygen as tetravalent, neither the reason nor the necessity for this is wholly apparent; the results could be equally well expressed by an ordinary bivalent form, and, indeed, the author is not consistent in the use of his tetravalent formulæ.

Ozone is without action on the trimethylene ring.

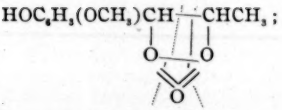
These ozonides are, in general, thick oils, or colorless, vitreous syrups, they have a characteristic, disagreeable odor and are more or less explosive. Some of them can be distilled under reduced pressure, others are resolved into their constituents when heated and the remainder explode. That they are peroxides is shown by their liberation of iodine from potassium iodide and their bleaching of indigo and potassium permanganate solutions. The most interesting reaction of the ozonides is, however, their behavior with water, in contact with which they yield hydrogen peroxide and aldehydes or ketones :



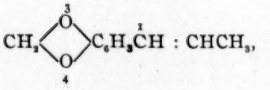
These reactions explain the production from isoeugenol,

$$HO\overset{4}{C}_6H_3(\overset{3}{O}CH_3)\overset{1}{C}H : CHCH_3,$$

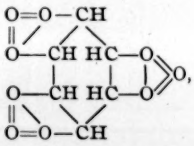
of vanillin by the action of ozone and water, the primary product being the ozonide, which decomposes in the manner indicated,



isosafrol,

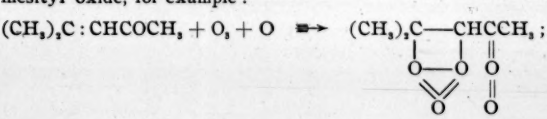


yields, in a similar manner, piperonal. With benzene the triozonide,

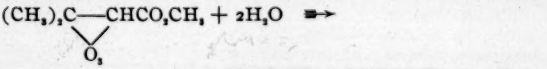


is formed which, with water, gives $3HCOCHO + 3H_2O_2$. It is many years since a more beautiful, purely chemical support for the Kekulé formula has been furnished.

Ethylene compounds containing a carbonyl group, *i. e.*, unsaturated aldehydes, ketones and monobasic acids, when treated with ozone, combine with 4 atoms of oxygen, as shown with mesityl oxide, for example :



with water the decomposition is similar to that already described,



In some cases the decomposition takes a different course, resulting in the production of peroxides, such as acetone peroxide, $(CH_3)_2CO_2$. This capacity of carbonyl derivatives to

decompose ozone, in contradistinction to the ability of the carbon atoms with an ethylene linkage to add it, is not confined to unsaturated aldehydes and ketones, heptoic aldehyde (œnanthol), $CH_3CH_2CH_2CH_2CH_2CHO$, for example, with ozone, yields the peroxide, $CH_3(CH_2)_5CH:O:O$, which is isomeric with heptoic (œnanthic) acid and, indeed, changes spontaneously into this in the course of time; with water the peroxide yields hydrogen peroxide and regenerates the original aldehyde. It is obvious that these facts are highly important and suggestive in connection with the current theory of the conversion of aldehydes into acids.

The action of nascent hydrogen on the ozonides is dependent on the proportion of the former; this is illustrated by methylheptenone ozonide, which, in ethereal solution, with aluminium amalgam, gives acetone and lævulinic aldehyde, or the corresponding alcohols, as follows:

$$(CH_3)_2C(O_2)CHCH_2CH_2C(CH_3)O_2 + 4H \rightarrow (CH_3)_2CO + OCHCH_2CH_2COCH_3 + 2H_2O,$$

and

$$(CH_3)_2C(O_2)CHCH_2CH_2C(CH_3)O_2 + 10H \rightarrow (CH_3)_2CHOH + HOCH_2CH_2CH_2CH(OH)CH_3 + 2H_2O.$$

The preceding facts make it easy to understand some of the results obtained by earlier workers, such as the formation of formaldehyde and formic acid from ethylene and ozone, and it is possible to correct certain statements which have found their way into the literature; thus, the ozone derivative of benzene is, as has been stated, $C_6H_6O_9$ and not $C_6H_6O_6$.

Ether appears to be capable of absorbing an unlimited quantity of ozone, the product is a viscid, colorless liquid, which may be distilled under reduced pressure, but which often explodes with terrific violence. These explosions are, apparently, spontaneous. No formula can be assigned to this substance, as the analytical results were very variable, but it certainly contains much more oxygen than the simple ozonide, $(C_2H_5)_2O(O_3)$. This property doubtless accounts for the violent explosions which occur from time to time during the distillation of ether, in circumstances where all suspicion of

the ignition of an ether vapor—air mixture is excluded, for we know that ozone is produced in the laboratory by various processes which are operative there.

By means of ozone Harries has succeeded in preparing, with ease, a number of interesting compounds which were either previously unknown or difficult to obtain; the list includes lævulinic aldehyde, $CH_3COCH_2CH_2CHO$, from methylheptenone; aminoacetaldehyde hydrochloride, $OCHCH_2NH_2.HCl$, from allylamine hydrochloride; succinic dialdehyde, $OCHCH_2CH_2CHO$, from diallyl; methylglyoxal, $OCHCOCH_3$, from mesityl oxide, and mesoxaldialdehyde, OCHCOCHO, from phorone.

One of the most interesting sections of Harries' paper is that which deals with the results of his efforts to apply the ozonide reaction to the determination of the constitution of various compounds. Space will not permit of details being given, but the ground for his conclusions will be readily understood by the contents of the preceding paragraphs. The phenylbutene obtained from 1-phenyl-3-aminobutane,

$$C_6H_5CH_2CH_2CH(NH_2)CH_3,$$

proves to be a mixture of 1-phenylbutene(1),

$$C_6H_5CH : CHCH_2CH_3,$$

and 1-phenylbutene (2),

$$C_6H_5CH_2CH : CHCH_3,$$

because it yields a mixture of benzaldehyde and phenylacetaldehyde. Diallyl must contain its ethylene linkage in the 1,5-position, because it yields succinic dialdehyde,

$$OCHCH_2CH_2CHO.$$

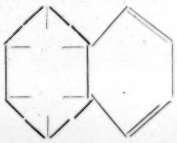
The hydrocarbon formed from magnesiummethyl iodide and diethyl succinate is 2,5-dimethylhexadiene(1,5),

$$CH_2 : C(CH_3)CH_2CH_2C(CH_3) : CH_2,$$

because it yields formaldehyde and acetonyl acetone. Dimethylheptadiene is $(CH_3)_2C : CHCH_2CH_2C(CH_3) : CH_2$, because it yields lævulinic aldehyde and, for the same reason, the fundamental hydrocarbon of caoutchouc has the identical grouping, *viz.*, $>CHCH_2CH_2C(CH_3)<$. Crotonic and isocrotonic acids, $CH_3CH : CHCOOH$, must have the same constitution because both yield acetaldehyde and glyoxalic acid, and a similar relation is proved to be true of oleic and elaidic acids,

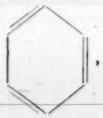
$CH_3(CH_2)_7CH : CH(CH_2)_7COOH$, each of which gives nonylic aldehyde, $CH_3(CH_2)_7CHO$, and the half aldehyde of azelaic acid, $OCH(CH_2)_7COOH$. The results with compounds of the terpene series were not so simple and are being further investigated.

The action of ozone on benzene has been described earlier in this report. Mesitylene, in a similar manner, yields methylglyoxal, CH_3COCHO. From naphthylene a diozonide is formed which yields phthalic dialdehyde, $C_6H_4(CHO)_2$, and, probably, glyoxal; this is regarded as supporting Baumberger's formula for naphthalene,

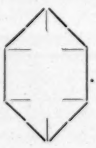


according to which one ring is "aliphatic" and the other "aromatic." Phenanthrene behaves in a manner similar to naphthalene, but anthracene could not be investigated on account of its insolubility. Diphenyl gives a tetraozonide.

The author suggests that those aromatic compounds which react with ozone probably have ethylene linkages in the nucleus.



whereas nitrobenzene, chlorobenzene, phenol ethers, acids, esters, etc., which are indifferent to ozone, are represented by the centric formula



The paper is extremely interesting and well worth the study of all chemists. J. BISHOP TINGLE.

The Physical and Chemical Properties of Iron Carbonyl.

There has recently[1] appeared, under the above title, a paper by Sir James Dewar and Dr. Humphrey Owen Jones, which forms a sequel to those by the same authors on nickel carbonyl.[2] Attention is directed more particularly to the differences in formula, color, stability and, especially, in behavior toward light between the analogous compounds of iron and nickel.

Iron pentacarbonyl was discovered in 1891 by Mond and Quincke,[3] and was shortly afterwards isolated and studied by Mond and Langer,[4] to whom our knowledge of this remarkable substance is almost entirely due. This is owing, no doubt, to the great difficulty in obtaining the compound in quantity sufficient for investigation, a drawback which has not yet been overcome.

Iron carbonyl is a yellow liquid, the color being retained even after careful purification and drying; its formula is $Fe(CO)_5$, as proved by analyses and molecular weight determinations.

The vapor of iron pentacarbonyl was found to decompose quietly, without explosion, when heated to high temperatures alone, or in an inert gas. In general, its chemical reactions are exactly parallel with those of nickel carbonyl, differing only in their rapidity, which is much less owing to the greater stability of the iron compound. There are, however, some exceptions to this behavior.

The most striking difference between the two compounds is the decomposition of the iron derivative by light. This was observed by Mond and Langer, who gave to the solid product of decomposition the formula $Fe_3(CO)_7$, but their compound was not pure.

Dewar and Jones observd that, when pure, this solid substance shows no change upon exposure to dry air, and is only slowly affected by ordinary air; but that, if the decomposition of the liquid carbonyl is incomplete and the solid is contaminated with the liquid compound, it often takes fire.

By exposure of the ether or petroleum ether solution of the liquid carbonyl to light, pure crystals of the solid carbonyl were obtained as beautiful, lustrous, hexagonal, orange col-

[1] P. Roy. Soc., **76**, 558 (1905). Chem. News, **93**, 1, 14, 24 (1906).
[2] P. Roy. Soc., **71**, 427 (1903). J. Chem. Soc., **85**, 203, 213 (1904).
[3] J. Chem. Soc., **59**, 604 (1891).
[4] *Ibid.*, **59**, 1091 (1891).

ored plates. An analysis and a study of the liquid carbonyl established the formula $Fe_2(CO)_9$ for these crystals.

Upon being heated to 100° the nonacarbonyl decomposes according to the equation :

$$2Fe_2(CO)_9 = 3Fe(CO)_5 + Fe + 3CO.$$

Of considerable interest are the solutions of iron carbonyl in nickel carbonyl. These exhibit a much paler yellow color than solutions of equal concentration in other solvents. Moreover, light does not cause decomposition of the iron carbonyl when it is in dilute solutions in nickel carbonyl. To account for these facts the authors suggest the formation of an unstable compound,

$$Fe(CO)_5 + Ni(CO)_4 = FeNi(CO)_9.$$

E. J. HOFFMAN.

REVIEWS.

ÉTUDE GÉNÉRALE DES SELS. Par ALFRED DITTE, Membre de l'Institut, Professeur de Chimie a l'Université. Premièr Partie, Sels Binaires. Prix, 10 Francs. Deuxième Partie, Sels Ternaires Oxygénés. Prix 12 Francs 50. Paris : Dunod et Pinat. 1906.

These beautifully printed volumes are, perhaps, the most important recent contribution to the general literature of inorganic chemistry. Especially is the first volume important. Much of the chemistry of binary compounds is recent and is not found in text-books. Most of this new work is from Moissan and his pupils, often done with the help of the electric furnace at very high temperatures, or at extremely low temperatures with the agency of liquid air. Hitherto, knowledge of this work had to be pieced together from scattered, brief articles in the *Comptes rendus*. In this first volume—a large book of 304 pages—the author considers, in detail, the following binary series : Hydrides, fluorides, chlorides, bromides, iodides, cyanides, oxides, sulphides, selenides, tellurides, nitrides, phosphides, arsenides, antimonides, carbides, silicides and borides.

If the reader realizes that he, like most other chemists, really knows nothing of half of the compounds on this list, and that Ditte devotes 13 pages to hydrides, 18 to fluorides, 14 to cyanides, 9 to selenides, 16 to nitrides, 20 to carbides, etc., it is clear that here is something to be studied by older chemists as well as by advanced students, and that here the material, hitherto accessible only to those who could consult large libraries, is offered to the chemist in clear, well-classified form.

The second volume, of 383 pages, is in two sections. In the first the subjects are: General properties of salts, the action of heat, of light, of electricity upon salts, the action of the inherent mechanical energy of salts (explosives and explosion waves), the action of metals, of water, of other liquids than water, of oxidizing and reducing agents on salts, the reciprocal action of acids, bases and salts (theories of affinity), the action of acids, of bases and of salts upon salts. In the second section the author applies these studies to definite classes of salts: Nitrates, chlorates, sulphates and carbonates are the series chosen.

Those not accustomed to reading French books on inorganic chemistry will be struck by the fact that every chemical change is expressed—every equation written—in the terms of Berthelot's thermochemical system, and that no mention whatever is made of ions or electrolytic dissociation in the first volume, and in the second volume in two places only; first in a few absolutely necessary lines to explain the action of electric currents on bases and salts, and second in the admirably clear chapter on the action of water on salts, which includes the properties of solutions. Here 40 pages are given to the work of Faraday, Raoult, Coppet, Arrhenius, Jones, Nernst, Abegg and Loomis.

Still less will the structural chemist find his accustomed diet. In the chapter on sulphates the only reference to the subject of water of crystallization and water of constitution, or tetrahydroxylsulphuric acid, is the brief, bald statement, without data, that water combines with many sulphates to form hydrates which lose the water at varying temperatures, leaving anhydrous sulphates.

It is instructive to see how nicely a structuralist, an ionist, or a thermochemist can severally express the same facts, each ignoring all of the sacred dogmas of the other two, and calling especial—often exclusive—attention to those properties which are brought into relief by his views, or which bring his views into relief. For a layman the thermochemical view is, perhaps, the easiest of the three to crudely understand, on account of the incessant harping on thermal values only. This is very convenient as regards this book, for it enables the structuralist or ionist, who is quite unfamiliar with the Berthelot brand of thermochemistry, to get at the more important facts, postponing theories until some one of his own school may rewrite the material in terms of the desired theory.

A quotation from Vol. II., page 3, illustrates the French

point of view. The author has spoken of Gerhardt and his type theory.

". . . Following the discovery of the polyatomicity of phosphoric acid, glycerin, the sugars, etc., Gerhardt's disciples were led to resurrect the theory of radicals, treating it in an extraordinary way; to explain this curious property they imagined the existence of fictitious, unsaturated radicals—hydroxyl, carbonyl, sulphuryl, etc., and soon extended the idea of saturation or atomicity to the elements themselves, which were classified as mono-, bi- and triatomic. Typical formulas gradually gave place to so-called constitutional formulas, in which figure imaginary bonds between different elements and different hypothetical radicals.

" *The formulas of salts represent nothing further than one of their modes of generation.*

" All these metaphysical considerations have but a secondary interest from the point of view that the study of chemistry should not lie in discussing properties lying outside of the sphere of verified observation . . . . No method of writing the formula of a salt can indicate the inner structure, *for this escapes us, if, indeed, it exists.* A salt, like any other object, is a form of matter—nothing more, nothing less. If we write sulphate of zinc SO_4ZnO, we are expressing the fact that the easiest way to make it is by the action of sulphuric acid on zinc oxide; and when we write SO_3 sol. $+$ ZnO sol. $=$ $SO_3.ZNO$ sol. $+$ 41.3, we express, apart from all theory, the experimentally proved fact that, in passing from the system formed by solid sulphuric acid and solid zinc oxide to the solid sulphate of zinc, one must modify the velocity of these first two forms of matter so as to make them lose an amount of energy measured as 41.3 calories, and that, in consequence, the sulphate of zinc differs from the mixture of acid and base *solely and alone by this loss of 41.3 calories.* . . . . The formula SO_4Zn expresses the fact that this sulphate may be made by combining sulphur, oxygen and zinc in the indicated weight—proportions, and the equation $S + O_4 + Zn = SO_4Zn$ sol. $+$ 229.6 expresses the experimentally proved fact that solid sulphate of zinc differs from the system which represents the sum of its component elements solely and alone through a loss of energy measured by 229.6 calories."

To the reviewer, and doubtless to others trained in the Kekulé school, such ideas are unacceptable and, indeed, revolting; let us remember that the French chemist finds carbonyl and hydroxyl revolting, and that men trained to think in the French school have found in these views the stimulus

to work of the very highest permanent value. To us there is an undoubted benefit in approaching a known subject by a new road.

In these volumes of Ditte we find the scholarly treatment of the subject, the limpid clarity of diction and the complete literary finish which we have learned to expect from men of science in France. E. R.

LABORATORY EXPERIMENTS TO ACCOMPANY OUTLINES OF INORGANIC CHEMISTRY. By FRANK AUSTIN GOOCH, Professor of Chemistry in Yale University, and CLAUDE FREDERIC WALKER, Teacher of Chemistry in the High School of Commerce of New York City. New York: The Macmillan Co. 1905. Price, 50 cents.

This is an interleaved manual and note-book to be used with Gooch and Walker's "Outlines of Inorganic Chemistry," which was recently reviewed.[1] E. R.

HANDBOOK OF METALLURGY. By C. SCHNABEL. Translated by H. LOUIS. Vol. I. London and New York: Macmillan & Co., Limited. 1905. Price, $6.50.

In the study of non-ferrous metallurgy the English-speaking student has always been at a disadvantage in comparison with the French, and especially the German, in that he had to work without a book covering the subject adequately. As the standard German handbook of the late Bruno Kerl appeared as early as 1881, even Germans had to content themselves with the smaller publications of Balling and Pufahl to cover the more recent developments of practice until Schnabel published his two-volume "Handbuch der Metallhüttenkunde" in 1894 and 1896. This was translated by Louis and brought out in 1898 and . . . . . Of this revised and enlarged German edition of 1901–1903, the translation of Vol. I., the subject of the present review, has been again brought out by Louis. It covers the metallurgy of copper, lead, silver and gold. Volume II., treating of the minor metals, is promised for 1906. A student accustomed to follow the literature of non-ferrous metallurgy fails to find much that is new in reading Schnabel's manual; on the contrary, he sees little more than what he has become familiar with in other books. While this is a disappointment, the book, nevertheless, deserves praise because the principles of the various processes and operations are brought out clearly and their applications discussed by numerous examples from practice. The matter is well arranged, classification has, perhaps, been carried a little too far, and there may be too much repetition. The work has proved itself to be acceptable and to meet a certain demand, as is shown by the issue

[1] THIS JOURNAL, 34, 588 (1905).

of a new edition after a comparatively short interval of 7 years. The English volume has grown from 876 to 1090 pages; of this increase, 95 pages fall upon copper, 27 upon lead, 45 upon silver and 57 upon gold. The translation is all that could be desired. As to the size of the book, it appears to be too short to be exhaustive and too long to represent an ordinary text book. Authoritative criticism could not well be expected, as the time has passed when a single author could write a critical handbook on non-ferrous metallurgy. The future belongs rather to the compilers who, with the references, bring together all available facts leading to the first sources of information, and to the specialists who critically review all that is known in their several fields.

The German book, as it stands, supplements, to a certain extent, the treatise of Kerl; the translation, representing the only work of the kind, has the field to itself.

H. O. HOFMAN.

DIE MIKROSKOPIE DER TECHNISCH VERVENDETEN FASERSTOFFE. Bearbeitet von DR. FRANZ RITTER v. HÖHNEL. 2te Auf., pp. 248, mit 94 Holzschnitten. Wien u. Leipzig: Hartleben. 1905.

The first edition of this work, which appeared in 1887, was one of the earliest attempts to systematize and co-ordinate the scattered papers bearing upon the microscopic characteristics of those fibers having industrial uses, and included the individual investigations of the author himself. These had largely extended our knowledge of the subject at that time, but the improvements in microscopical methods, together with the appearance of various new fibers in the arts during the 18 years since the earlier edition, has made an extended revision necessary. The use of polarized light and the study of the dichroitic properties, aided by more numerous and better methods of staining, have added materially to the knowledge of the structural characteristics of many fibers, and the microscope has acquired increased importance in the technical examination and valuation of textile and other products.

The subject is considered under three heads: Vegetable Fibers, Animal Fibers, Wool and Hairs and Silks. In the 6 pages of introduction the scope of the work is outlined, and notes are given concerning the necessary instruments and reagents required for the study of fibers. Then follow about 24 pages of general statements concerning vegetable fibers, their morphological character, their microchemical and microphysical properties, and 2 tables showing the lengths and diameters of all the common vegetable fibers. In the next section the general structure of wool and hair is considered, together with the

methods of study and microchemistry and, lastly, the special examination of the individual species. Some 15 animal fibers are described and illustrated. The chapter on silk, following the same general scheme of treatment, consists almost wholly of the results of investigations by the author, previously published, in part, in "Dingler's polyt. Journal," **246**, 465.

The author holds that a mere description of a fiber is not sufficient to identify it with certainty, the real distinguishing features often being not superficially noticeable, but recognizable only by careful and painstaking *comparisons*. The precautions necessary in observation and treatment of fibers under examination are clearly set forth, with descriptions, illustrations and comparisons of the industrially important fibers. Throughout the entire text the cuts, 94 in number, are of noticeable clearness in outline and detail, and appear to be from drawings made from the *camera lucida*. But the clearness and simplicity of the *camera lucida* picture is rarely observed in the actual microscopic field, where broken and crushed particles of fibers, indefinite masses of mucilaginous or protoplasmic matter, starch granules, epidermal and parenchyma cell tissue, lignified tissue and other bodies often become disturbing and obscuring factors in the study of the particular fiber sought. With the great improvement in modern photographic methods and the highly finished papers of to-day, at least a few photomicrographs and illustrations of polarized light effects would have added to the value of the work. The book will be of much assistance to microscopists and chemists having to deal with textile problems involving the identification of fibers.

F. H. THORP.

A TEXT-BOOK OF CHEMISTRY FOR THE USE OF STUDENTS AND PRACTITIONERS OF MEDICINE, DENTISTRY AND PHARMACY. By WILLIAM RUSSELL JONES, M.D., PH.G., Professor of Medical Chemistry and Toxicology, and Lecturer on Medical Diagnosis in the University College of Medicine, Visiting Physician to the Virginia Hospital, Richmond, Virginia. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1905. Price, $2.50.

This volume is broad in scope. An introduction on the properties of matter is followed by a section on physics, 55 pages, giving elementary notions of gravity, heat, light and electricity. Then comes chemical philosophy, 23 pages; inorganic chemistry and qualitative analysis, 149 pages; organic chemistry, 125 pages; quantitative analysis, 5 pages; and physiological chemistry, 70 pages; a total of 448 pages.

The treatment is necessarily brief and elementary, but it is clear, and the book really includes what is necessary for dentists and pharmacists and for the average student of medicine.

It seems to the reviewer that the comprehensive plan of the book is very suitable, and that the chance of the average student acquiring a little definite knowledge of the different subjects is greater than if he were given separate text-books containing matter which he probably could not understand and certainly could not master in the time available. E. R.

TEXT-BOOK OF MEDICAL AND PHARMACEUTICAL CHEMISTRY. By ELIAS H. BARTLEY, B.S., M.D., PH.G., Professor of Chemistry, Toxicology and Pediatrics in Long Island College Hospital, etc. Sixth edition. Philadelphia: P. Blakiston's Son & Co. 1906. pp. 774. Price, $3.00 net.

The author here presents a work dealing with the entire field of chemistry—organic, inorganic, physiological and theoretical. In addition to this, 67 pages are devoted to elementary physics. Those substances of medical and pharmaceutical interest are considered in greater detail, and often a brief statement of the physiological action is given. Under the important poisons the symptoms, antidotes and method of treatment are detailed. Several errors were noted in the book. Thus, the author defines an atom as "the smallest conceivable portion of matter." To this he adds the correct definition, but the student would have already received the wrong impression. Again, he states that "nitrogen may be tested for (in organic substances) by burning the substance in air, when, if nitrogen be present in more than traces, it will give off an odor like burning feathers or horn."

The arrangement is often very illogical indeed. Thus, in the part on organic chemistry, which consists of about 200 pages, the carbohydrates are considered and their structure given before the simple aldehydes and ketones have been described. The work may be of value, as a reference book, to physicians and pharmacists who must be satisfied with a single book on all chemical matters. A. S. L.